ERRATA

page 20, line 24: insert "Environmental" after "US"
page 37, line 6: delete "tye", insert "tyre"
page 39, fourth line up: delete "pollution", insert "pollution" after "water"
page 40, bottom line: delete "173", insert "1973"
page 52, line 7: delete "ratio", insert "ratios"
page 81, line 31: delete "samples", insert "samplers"
page 83, line 33: delete "parallel", insert "perpendicular"
page 91, bottom line: insert "All samples were measured." after "... water."
page 92, line 22: delete "0.5", insert "0.45"
page 106, line 24: delete "$^{56}$Min", insert "$^{56}$Mn"
page 173, line 14: delete "lead", insert "load"
page 190, Table 5.12: delete "Indpendent", insert "Independent"
page 193, Table 5.13: delete "Indpendent", insert "Independent"
page 207, line 24: delete "course", insert "source"
page 217, line 35: delete "from sample 2", insert "from sample 1"
page 221, line 26: delete "p", insert "P"
page 234, line 8: insert "a" after "to"
page 234, line 9: end sentence after "data", delete remainder
page 240, line 20: insert "some" after "in"
page 253, line 24: delete "13.4", insert "36"
page 308, eight lines up: delete "courses", insert "sources"
page 309, line 41: delete "103°", insert "110°"
page 310, line 7: insert "and flame" after "flameless"

# BROMIDE, LEAD AND OTHER CONTAMINANTS WITHIN A MOTORWAY CATCHMENT

by

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A thesis submitted to the University of London
in partial fulfilment of the requirements for the
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# Bromide, Lead and Other Contaminants within a Motorway Catchment

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C.J. Sollars

## ABSTRACT

The water quality problems related to stormwater runoff from urban and road surfaces and the options available for motorway runoff treatment have been reviewed. In particular, the potential of road runoff for contributing to the bromide content of surface waters has been surveyed in the context of widespread concern over the detection of brominated trihalomethanes in some potable water supplies.

Stormwater runoff quality from a length of the M1 motorway has been examined in terms of a number of chemical and physical parameters over an eleven-month period. Concentrations of many parameters examined varied by up to two orders of magnitude during this period, and most overall variation was noted for those affected by application of de-icing salt during winter months. This was considered to be the most significant seasonal factor affecting runoff quality generally, but seasonal differences in storm characteristics were also found to be important in this respect.

Total suspended solids, lead, cyclohexane-extractable organic content, polynuclear aromatic hydrocarbons, chloride and bromide were the runoff contaminants whose concentrations were considered to give cause for the greatest environmental concern. De-icing salt impurities were found to be potentially significant contributors to total suspended solids, bromide and possibly cadmium runoff loads, while tyre wear products were estimated to contribute the majority of zinc loads and possibly a substantial proportion of cadmium loads. Comparison of the effluents from a french drain and sedimentation tank receiving untreated runoff from the same site indicated that the french drain was more effective than the sedimentation tank at removing total suspended solids and solid-associated contaminants.

Bromide concentrations in runoff were found to be up to one hundred times greater than reported surface water background values. Particulate vehicle emissions were found to be the main bromide source on an annual basis, while de-icing salt contributed up to 35% of the winter runoff load. A significant decrease in the bromide/lead ratio in deposition and road surface dust compared with roadside ambient air values was observed, which was attributed to bromide loss by volatilisation or leaching from deposited particulates. In contrast to lead, relatively rapid solubilisation of bromide from the road surface occurred during individual events, leading to more effective removal of bromide than for lead, which in turn led to bromide/lead ratios in runoff often considerably higher than in air or deposition. Runoff bromide loads in summer were significantly affected by the length of antecedent dry period, and a bromide deposition rate derived from runoff data was in good agreement with measured values. Estimated surface water bromide concentrations arising from motorway runoff at some points of potable supply abstraction in the UK approached values previously reported to lead to brominated trihalomethane formation during chlorination.

To Gertrud, Ian and Ben

with grateful thanks

for their support and patience

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## LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| AAS | atomic absorption spectrophotometry |
| BOD | biochemical oxygen demand |
| BSI | British Standards Institution |
| cm | centimetre |
| COD | chemical oxygen demand |
| concn | concentration |
| EC | electrical conductivity |
| EEC | European Economic Community |
| FD | french drain |
| FWM | flow-weighted mean |
| Fig. | figure |
| g | gram |
| h | hour |
| ID | internal diameter |
| INAA | instrumental neutron activation analysis |
| keV | kiloelectron volt |
| kg | kilogram |
| km | kilometre |
| l | litre |
| m | metre |
| mg | milligram |
| min | minute |
| ml | millilitre |
| mm | millimetre |
| n | neutron |
| NAA | neutron activation analysis |
| ng | nanogram |

| | |
|---|---|
| nm | nanometre |
| PAH | polynuclear aromatic hydrocarbon |
| pH | hydrogen ion concentration |
| PVC | polyvinyl chloride |
| s | second |
| ST | sedimentation tank |
| THM | trihalomethane(s) |
| TRRL | Transport and Road Rseearch Laboratory |
| TS | total solids |
| TSS | total suspended solids |
| TVS | total volatile solids |
| UK | United Kingdom |
| ULRC | University of London Reactor Centre |
| US | United States |
| UTR | untreated runoff |
| WHO | World Health Organisation |
| WRC | Water Research Centre |
| yr | year |
| µg | microgram |
| µl | microlitre |
| µm | micron |
| µS | microsiemen |

## SECTION 1. INTRODUCTION

A reliable supply of potable water and efficient disposal of wastewaters are fundamental prerequisites of modern, high population density urban communities. In many parts of the world, however, increasing populations and industrial development place ever larger demands on an essentially finite water supply (Bachus, 1974).

In developed countries, one aspect of this problem is the increasing need to turn to lowland rivers as additional sources of water supply for cities, in contrast to previous general practice of building upland impoundments or utilising groundwater resources. Lowland sources have the disadvantage, however, of often being of poor quality, due to accumulated contaminant loads from upstream point source discharges (e.g. sewage works and industrial effluents) and non-point sources, which include agricultural and urban runoff. Until recently, however, point sources have been regarded as the main source of pollutants, and, because of this, considerable progress has been made in recent years in many of the developed countries in controlling and reducing major point source effluents (Whipple and Hunter, 1977; Carter, 1985). Nonetheless, this progress has often served to reveal that, to obtain many water quality objectives, non-point sources must now be given the same degree of attention as point sources. In the United States (US), for instance, recent surveys have established that almost all of the states acknowledge that they have a non-point water pollution problem, and in 25 the problem is characterised as "major" (Carter, 1985), while the US Protection Agency (EPA) has estimated that about 50% of the nation's water pollution can be attributed to non-point sources (Ahmed and Schiller, 1980). In general, surface runoff from urban areas and areas of agricultural use is considered to be the most seriously contaminated.

As a specific example of the effects of urban runoff quality in undermining a point source improvement programme, Randall and Grizzard (1983) cited the case of the Occoquan Reservoir in the suburbs of Washington, DC, an indispensible water supply for 650,000 people in the area. During the 1960's, the quality of water in the reservoir began to deteriorate rapidly, and an extensive programme of point source pollution control was implemented to remedy the situation. As this programme progressed, however, it was observed that although the

amount of pollution from point sources had greatly decreased, the quality of the water continued to worsen. Extensive monitoring revealed that the main cause of this pollution was stormwater runoff from the rapidly urbanising catchment above the reservoir. Thus the benefits of point source control had been completely nullified by the water quality impact of urban runoff.

Such experiences have generated an increasing awareness that urbanisation greatly increases the levels of pollutants that reach streams and other bodies of water in the area concerned, and this awareness is reflected in the very large number of studies of urban runoff quality which have been undertaken in many parts of the world in recent years. The results of many of these were collated by Pope (1980) and a summary of the data reviewed is presented in Table 1.1. Precipitation quality data from the same source are also included for comparative purposes.

The data reflect one of the singular characteristics of urban runoff - namely, the very wide range of concentrations which can be encountered, which can extend over two or three orders of magnitude. This almost certainly reflects the great diversity which can exist in catchment characteristics in terms of their hydraulic and hydrological nature and the great variety of potential runoff pollutant sources. It is this characteristic which, coupled with the unpredictable nature of storm flows, makes urban runoff quality assessment and control a much more difficult task than managing a relatively predictable and continuous stream of domestic or industrial effluent entering a treatment plant (Harrop, 1983). Table 1.1 also demonstrates that for many parameters, precipitation may make a significant impact on final quality, although there is a frequent failure in the literature to clarify whether precipitation data presented refers to both wet and dry deposition combined or to rainfall only. Thus the actual contribution of rainfall itself before contact with the ground may not always be as significant as precipitation data indicate, even if "stripping out" of atmospheric pollutants has taken place. The frequent ambiguity concerning these two aspects of atmospheric deposition in the literature often complicates evaluation of its contribution to urban runoff quality.

TABLE 1.1 : Summary of a range of parameters and concentrations found in urban runoff and precipitation (after Pope (1980) and references therein)

| Parameter | Reported Concentration Ranges ($mgl^{-1}$) | |
|---|---|---|
| | Precipitation | Urban Runoff |
| COD | 2.5-322 | 5-3100 |
| BOD | 1.1 | 1-700 |
| Total solids | 18-24 | 400-15320 |
| Volatile total solids | - | 12-1600 |
| Suspended solids | 2-13 | 2-11300 |
| Volatile suspended solids | 6-16 | 12-1268 |
| Settleable solids | - | 0.5-5400 |
| Total dissolved solids | - | 9-574 |
| Volatile dissolved solids | - | 160 |
| Conductivity (μS) | 8-395 | 5.5-20000 |
| Turbidity (JTU) | 4-7 | 3-70 |
| Total organic carbon | 1-18 | 14-120 |
| Total inorganic carbon | 0-2.8 | 1-17 |
| Oils/hydrocarbons | - | 0-110 |
| Phenols | - | 0-10 |
| Total nitrogen N | 0.5-9.9 | 1.1-6.2 |
| Organic N | 0.1-0.32 | 0.1-16 |
| Inorganic N | 0.69 | 1.0 |
| Ammonia N | 0.01-0.4 | 0.1-14.0 |
| Nitrate N | 0.02-5.0 | 0.1-2.5 |
| Nitrite N | 0-0.1 | 0-1.5 |
| Total phosphorus | 0.001-0.35 | 0.09-4.4 |
| Hydrolysable phosphorus | 0.8-0.24 | 0.1-10 |
| Chloride | 0.1-1.1 | 2-25000 |
| Cadmium | 0.013-0.056 | 0.006-0.045 |
| Chromium | 0.023-0.08 | 0.01-27.0 |
| Copper | 0.06-0.48 | 0.041-0.45 |
| Iron | 0-3.05 | 0-5.3 |
| Lead | 0.024-10.4 | 0.01-14.5 |
| Mercury | - | - |
| Nickel | - | - |
| Zinc | 0.02-4.9 | 0.01-5.23 |

As previously noted, the range of concentrations in Table 1.1 reflect the fact that a multiplicity of sources affect urban runoff quality. Apart from the quality of precipitation itself, which may be especially contaminated in urban areas due to atmospheric pollution,

overland flow resulting from precipitation will accumulate pollutants from a variety of surfaces, such as roads, roofs, driveways, pavements and other impermeable areas and, to a far lesser extent, grassed and unpaved areas (Pope, 1980). In addition, the final outfall quality will also be affected by chemical and physical changes within drainage systems employed to carry stormwater to a treatment works or direct to a receiving water (Ellis, 1977), but in terms of the original input to the drainage system, land use in the catchment concerned will be expected to have an important impact on runoff quality.

A basic problem in quantifying urban land use effects is categorising land uses into distinct groupings, but a widely accepted broad classification for urban areas is residential, industrial and commercial, adopted by Sartor and Boyd (1972) in their extensive study of street surface contaminants. They found that although considerable variation existed between land use categories, the solids loading per unit area was found to increase in the order commercial < residential < industrial. This was attributed to a combination of infrequent sweeping and heavy use in industrial areas, in contrast to the much more regular sweeping frequently found in commercial areas. Broadly similar trends were found for nutrients and metals. Harrop (1983), however, in reviewing the literature concerning land use-runoff quality relationships, noted that several authors had reported conflicting trends for some parameters, but that this was possibly largely due to the fact that comparisons were often made between similar land uses in entirely different catchments, whereas few studies of homogeneous land use areas within the same catchment had been reported.

Despite these complications, road surfaces will be a common feature of all urban land use areas, and some workers have attempted to assess their contribution to the total runoff loads from specific catchments. In a detailed study of a small residential catchment in the Stevenage area, the Water Research Centre (WRC) reported (1977) that, in terms of sources, pollutant masses exported from the catchment could be approximately apportioned between aerial deposition (25%), decay of roofing and guttering materials (3%) and road and pavement area contributions (72%). In particular, about 70% of total solids arose from the latter source (Mance and Harman, 1978).

Söderlund and Lehtinen (1972), in a study of three land use types in a Stockholm suburb (terrace housing, suburban shopping centre and a cloverleaf junction carrying 65,000 vehicles per day), found that the estimated annual surface runoff discharges (in kg $ha^{-1}yr^{-1}$) for a range of parameters (total solids, suspended solids etc.) were all greater for the highway catchment than for the other areas (Table 1.2). The authors pointed out that part of the reason for these higher loadings was the low permeability of the highway compared with the other two sites, and this is often an important factor in the context of the relative effects of different land use types on urban runoff quality, together with the significant percentage of urban areas which road surfaces occupy (Ellis, 1979).

Studies such as those of Söderlund and Lehtinen (op. cit.) have therefore increased awareness of the often highly contaminated nature of road surface runoff, and in addition the considerable extension of motorway networks in many countries in recent years has focussed particular attention on the water quality problems which this may create (Colwill et al., 1984) in both urban and rural areas.

## 1.1 Motorway Surface Runoff

### 1.1.1 Water Quality of Motorway Runoff

In contrast to most road surfaces in urban areas, motorways often incorporate discrete, well-defined catchments which receive little or no runoff from adjacent areas. In terms of examining specifically road-related effects on urban stormwater pollution, the advantages of such catchments are that extraneous effects on runoff quality not directly related to roads are minimised or excluded (Pope, 1980). This greatly enhances the possibility of specifically quantifying road-related contaminant concentrations and loadings in runoff and identifying some of the major contaminant sources and removal processes which determine the final discharge quality. The more extensive studies in terms of the range of parameters examined and project duration are those of Söderlund and Lehtinen (1972), Hedley and Lockley (1975), Dauber et al. (1978), US Federal Highway Administration (FHWA; 1981a), Cathelain et al. (1981) and Klein (1982), and a summary of data from these authors is presented in Table 1.3. In addition, results of an intensive UK study of runoff quality from the M1 in

TABLE 1.2 : Estimated annual discharges (kg $ha^{-1}yr^{1}$) in urban stormwater from three different catchment areas in Stockholm, Sweden (after Söderlund and Lehtinen, 1972)

(All data in units of kg $ha^{-1}yr^{-1}$)

| Sampling Areas | | TS | VDS | TSS | VSS | Hydro-carbons | Phosphorus | | Nitrogen | | Oil | BOD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $PO_4$ | Total | $NH_4$ | Total | | |
| Highway | (RC = 0.8) | 2040 | 605 | 1185 | 860 | 13.4 | 0.07 | 0.2 | 2.5 | 5.1 | 36 | 100 |
| Terrace houses | (RC = 0.2) | 470 | 68 | 173 | 120 | 2.6 | 0.01 | 0.04 | 0.4 | 1.4 | 0.1 | 14 |
| Residential blocks | (RC = 0.6) | 930 | 180 | 620 | 490 | 6.6 | 0.06 | 0.16 | 1.8 | 3.45 | 2.4 | 43 |

RC = Runoff Coefficient
TS = Total Solids
VDS = Volatile Dissolved Solids
TSS = Total Suspended Solids
VSS = Volatile Suspended Solids

TABLE 1.3 : Reported ranges of pollutant concentrations in road runoff

| Parameter | Söderlund and Lehtinen (1972) | | Hedley and Lockley (1975) | Dauber et al. (1978) | FHWA (1981a) | | Cathelain et al. (1981) | | Klein (1982) |
|---|---|---|---|---|---|---|---|---|---|
| ($mgl^{-1}$) | Mean[a] | Max | Range of monthly FWM's | FWM over 9 events | Mean[b] | Max | Mean[b] | Max | FWM over 145 events[c] |
| COD | | | - - | - | 14 | 1058 | 79 | 394 | 85.6 - 118.5 |
| $BOD_5$ | 36 | 90 | 4 - 64.5 | 12.2 | 24 | 133 | 8.9 | 35 | - - |
| Total solids | 855 | 2800 | - - | - | 1147 | 21640 | - | - | - - |
| Volatile total solids | 170 | 1630 | - - | - | 242 | 1522 | - | - | - - |
| Total suspended solids | 282 | 1000 | 134 2599 | - | 261 | 1656 | - | - | - - |
| Volatile suspended solids | 132 | 600 | 47 642 | - | 77 | 837 | - | - | - - |
| Total organic carbon | - | - | - - | 19.6 | 41 | 290 | - | - | - - |
| Dissolved organic carbon | - | - | - - | 7.1 | - | - | - | - | - - |
| Total oils/hydrocarbons | 58 | 100 | - - | - | - | - | - | - | 2.05 - 7.02 |
| Total PAH ($\mu gl^{-1}$) | - | - | - - | - | - | - | - | - | 2.51 - 2.97 |
| Total N | 2.1 | 4 | - - | - | - | - | - | - | - - |
| Nitrate N | - | - | - - | 1.3 | - | - | 8.2 | 25.2 | - - |
| Ammonia N | - | - | - - | 0.5 | - | - | 1.45 | 7.7 | - - |
| Total phosphorus | 0.08 | 0.3 | - - | 0.28 | 0.79 | 3.55 | - | - | 0.25 - 0.35 |

Table 1.3 continued

| Parameter | Söderlund and Lehtinen (1972) | | Hedley and Lockley (1975) | Dauber et al. (1978) | FHWA (1981a) | | Cathelain et al. (1981) | | Klein (1982) |
|---|---|---|---|---|---|---|---|---|---|
| ($mgl^{-1}$) | Mean[a] | Max | Range of monthly FWM's | FWM over 9 events | Mean[b] | Max | Mean[b] | Max | FWM over 145 events[c] |
| Chloride | 261 | 360 | 16 - 23670 | 159 | 386 | 13300 | 133 | 794 | 108 - 357 |
| Sulphate | - | - | - | 15 | - | - | 43.9 | 138 | - |
| Cadmium ($\mu gl^{-1}$) | - | - | - | 3.4 | 40 | 400 | - | - | 2.8 - 5.9 |
| Chromium | - | - | - | - | 0.04 | 0.14 | - | - | 5.2 - 20.4 |
| Copper | - | - | 0.1 - 1.44 | 0.047 | 0.10 | 0.88 | - | - | 0.058- 0.117 |
| Iron | - | - | 8.5 - 182.9 | - | 10.3 | 45 | - | - | 2.18 - 5.16 |
| Lead | 0.01 | 0.1 | 0.45 - 4.94 | 0.34 | 0.96 | 13.1 | 0.27 | 1.42 | 0.163- 0.245 |
| Mercury ($\mu gl^{-1}$) | - | - | - | - | 3.22 | 67.0 | - | - | - - |
| Nickel | - | - | - | - | 9.92 | 49.0 | - | - | - - |
| Zinc | - | - | 0.65 - 8.0 | 0.25 | 0.41 | 3.4 | 0.55 | 1.99 | 0.32 - 0.62 |
| Total metals | - | - | 1.39 - 15.01 | - | - | - | - | - | - - |
| Soluble metals | - | - | 0.53 - 6.24 | - | - | - | - | - | - - |

a = arithmetic mean of individual samples from 50 events
b = mean of flow-weighted mean concnetrations
c = 3 sites
FWM = flow-weighted mean (concentration)
FHWA = Federal Highway Administration

Bedfordshire have been published by the Transport and Road Research Laboratory (Colwill et al., 1984) but much of this was based upon results from the present work, and these are presented and discussed in Section 5.

Comparison between the studies presented in Table 1.3 is not always straightforward due to different ways of presenting data - these are noted in the table. The data has been arranged in parameter groups similar to those in Table 1.1 in order to facilitate comparison with general urban runoff quality. Despite difficulties arising from different modes of presentation, it is clear from comparison of the two tables that road runoff alone is potentially a dominant contributor to urban runoff pollutant concentrations. Such general comparisons are of limited use, however, and of those authors represented in Table 1.3, Dauber et al. (1978) and Klein (1982) have attempted to relate motorway runoff and domestic sewage loadings from residential areas in order to facilitate comparisons.

Dauber et al. used the concept of population equivalents, i.e. calculating the theoretical residential population density which would give rise to an annual or in-storm runoff loading for particular parameters equal to those found in their Swiss motorway studies. These values were compared to the mean Swiss population density of 37 persons $ha^{-1}$. The results are given in Table 1.4, from which it can be seen that, considered on an annual basis, stormwater quality parameters which are dominant in domestic sewage (e.g. BOD, ammonia etc.), make a below-average contribution, while for hydrocarbons, Pb, Cu and Cd, the population equivalents are several times greater than the average, especially for Pb, demonstrating the essentially vehicle-related nature of these pollutants. Considered on a duration of runoff basis, the contrast is even more pronounced, with only ammonia and total phosphorus from highway runoff making a below-average contribution. This latter basis of comparison underlines the very large pulse effect that receiving waters can potentially be subjected to from untreated road runoff during events themselves, while even on an annual basis, road runoff con pose specific hazards such as those from hydrocarbons and Pb.

TABLE 1.4 : Representation of runoff mass loads from N1 (Switzerland) as population equivalents (after Dauber et al., 1978)

| Parameter | Population Equivalent[a] of motorway (persons $ha^{-1}$) | |
|---|---|---|
| | Annual | Duration of Runoff |
| Total suspended solids | 19 | 230 |
| Total organic carbon | 9 | 110 |
| Dissolved organic carbon | 8 | 100 |
| Hydrocarbons | 190 | 2300 |
| $BOD_5$ | 5 | 63 |
| Lead | 1900 | 24000 |
| Zinc | 60 | 700 |
| Copper | 160 | 2000 |
| Cadmium | 340 | 4300 |
| Ammonia N | 1.4 | 18 |
| Total Nitrogen[b] | 5.7 | 71 |
| Total Phosphorus | 1.4 | 18 |

[a] = mean Swiss population density -37 persons $ha^{-1}$
[b] = defined as sum of nitrate - N and Kjeldahl N

Klein (op. cit.) carried out similar comparisons with data from his three motorway sampling sites in the Federal Republic of Germany (FRG), one of which contained a large (60%) pervious area. Excluding the latter, comparisons of annual runoff loadings (kg $ha^{-1}yr^{-1}$) with effluent from a sewage works treating domestic waste from 100 inhabitants showed that motorway runoff substantially exceeded sewage loadings for suspended solids, COD, Cu and Pb. On a duration of runoff basis, stormwater loadings for TSS, COD, Cd, Cu, Pb and Zn were between one and two orders of magnitude greater than treated domestic effluent, with TSS loads in particular being about ninety times greater. As with Dauber's study, only for ammonia nitrogen and total phosphorus were motorway loadings smaller than domestic on an in-storm basis. In addition to these comparisons, Söderlund and Lehtinen (1972) compared urban runoff in general with treated domestic effluent and found similar trends, with in-storm suspended solids loadings being 33 times greater than the equivalent from domestic effluent.

Although Klein (1982) did not present loading data for polynuclear aromatic hydrocarbons (PAH), concentrations of those (unspecified) found in motorway runoff were in the region of 50 to 60 times greater than in the effluent of a typical sewage works. Hoffman et al. (1984), in a comparative study of PAH runoff loadings from highway, industrial, residential and commercial land use areas in Rhode Island, USA, reported that highway and industrial land uses contributed substantially higher PAH loadings than the other land use types, while Gjessing et al. (1984) observed that PAH concentrations in streams receiving motorway drainage water near Oslo, Norway, were noticeably greater with respect to background values than metal concentrations. Harrison et al. (1975) have also noted that, during heavy rainstorms, the PAH concentrations in raw sewage may increase by up to 100-fold compared with dry weather conditions, due to the effects of urban ruoff.

The apparent potential of road runoff for introducing very substantial suspended solid loads into receiving waters is of particular significance, since it has been widely observed that many pollutants of concern are substantially solid associated in road runoff. Cathelain et al. (1981), for example, found that for COD, BOD, Pb and Zn, the settleable percentages were 51, 44, 98 and 64% respectively, while Pope et al. (1978a), in an earlier study of the M1 catchment used in this work, reported that 99% of the metal load and 85-90% of the oil and PAH load discharged was sediment associated. Klein (1982) noted similar trends for PAH. Hedley and Lockley (1975) reported that 77% of the total annual estimated metal load from their A38M catchment was solid associated. In a more general study of urban runoff, Collins and Ridgeway (1980) reported significant correlations between suspended solids and total organic nitrogen, ammonia, total phosphates, Pb and Zn, although oil and grease showed no strong correlation. Laboratory settlement studies on urban runoff samples by Whipple and Hunter (1981), however, indicated that 65% of hydrocarbons and 70% of TSS settled out in 32 h in undisturbed water, while Pb followed similar trends to TSS (60% settled). Biochemical oxygen demand, Cu, Ni and Zn generally showed more variable results and slower settlement.

High suspended solids loadings themselves can cause degradation of receiving water quality by physical burial of bottom dwelling

aquatic organisms and reduction in transparency leading to photosynthesis inhibition (Sartor and Boyd, 1972). These were among a range of possible effects of highway runoff on receiving waters cited by the FHWA (1981b), which also included aesthetic deterioration, dissolved oxygen depletion and accumulation of toxic materials (such as heavy metals or persistent organics) and adverse effects on potable water supplies. Effects such as these may be particularly important in rural catchments with unpolluted streams, but in the UK no extensive long term studies on this topic have been reported. Dussart (1984), however, examined the effect of M6 runoff on stream ecology in areas of Cumbria and Lancashire. Some adverse effects on macroinvertebrate species diversity were noted downstream of motorway drainage outfalls, but were not considered sufficient to warrant further study. Other authors consider, however, that long term studies are necessary to adequately assess the potential hazard from this source to aquatic life (Van Hassel et al., 1980), and an extensive FHWA study concerning a range of receiving water effects of highway runoff is at present in progress (Anon, 1985).

### 1.1.2 Sources of Motorway Runoff Contaminants

Figure 1.1 illustrates the main sources of contaminants ((a)-(f)) and removal processes affecting urban road surfaces. In a motorway catchment which receives no runoff from adjacent areas and where pedestrian access is restricted, sources (d) and (e) will be minimal and thus the main contaminant inputs will be vehicle-related sources, atmospheric deposition, de-icing activities and road surface erosion.

#### (a) Vehicle-Related Contaminants

Motor vehicles are the source of a wide range of contaminants to the road surface, and the following classification is based upon that suggested by Sartor and Boyd (1972):

(i) Exhaust emissions

(ii) Leakage of fuel, lubricants, hydraulic fluids and coolants

(iii) Fine particles worn off tyres, clutch and brake linings

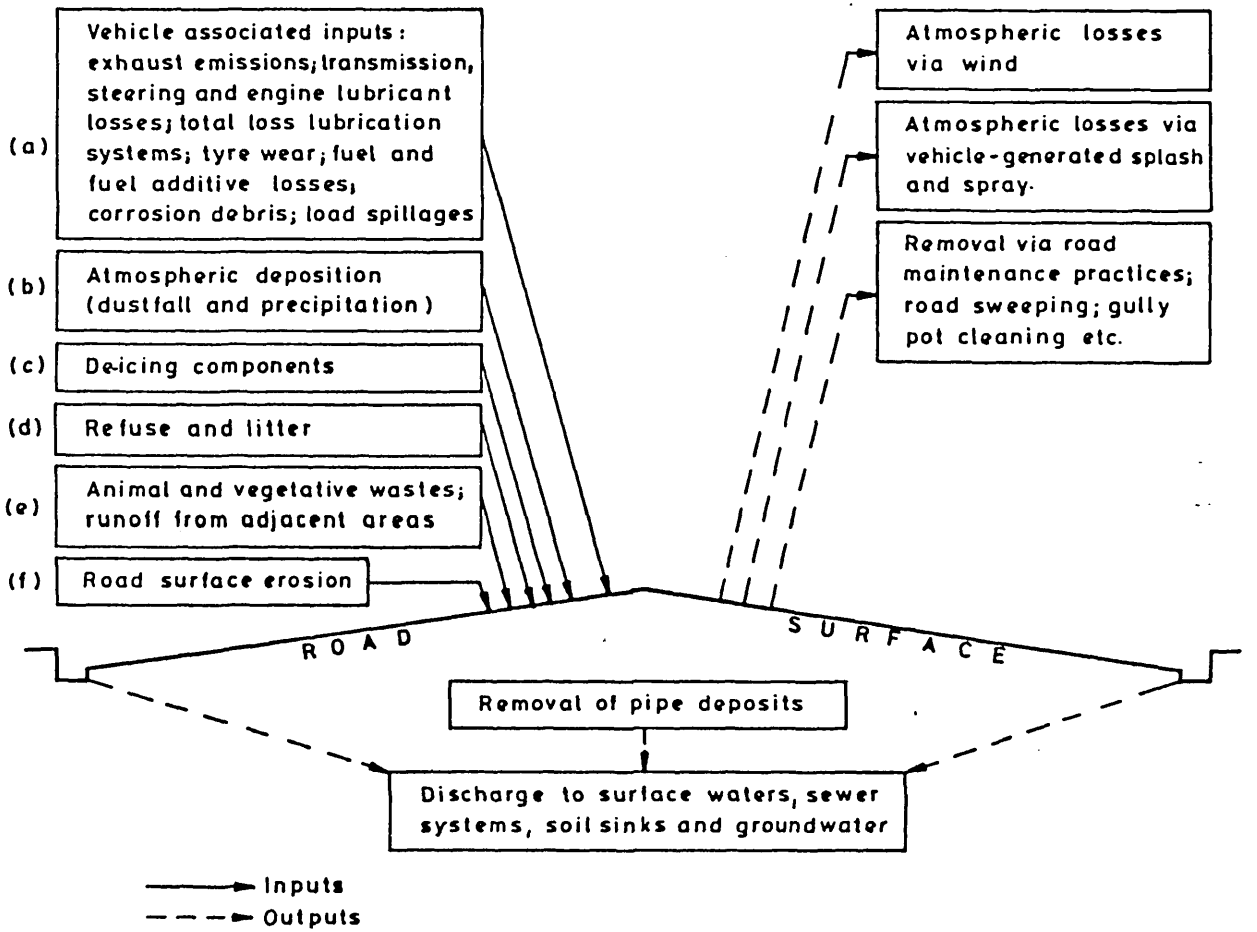



Figure 1.1 Contaminant sources and removal processes affecting an urban road surface (after Pope, 1980)

(iv) Dirt, dust and decomposing coatings which drop off vehicle trim linings, chassis and undercarriages; components broken by vibration or impact

(v) Spillage of vehicle loads

(i) Exhaust Emissions

Vehicle exhaust emissions are the source of a variety of pollutants, which may generally be classified as gaseous or particulate. The gaseous fraction consists mainly of carbon monoxide, nitrogen oxides, sulphur oxides and hydrocarbons (paraffins, naphthenes, olefins, aromatic and oxidised hydrocarbons) while the particulate fraction consists predominantly of carbonaceous particles, Pb compounds and particle-associated PAH (American Chemical Society, 1978; Watkins, 1981). In general, Pb and PAH, especially the former, are the exhaust components which have received most attention in terms of their contribution to motorway runoff quality.

Lead is present in petrol in the form of tetra-alkyl lead (TAL) compounds, principally tetramethyl lead (TML) and tetraethyl lead (TEL). In most European countries and the USA these are almost always present in conjunction with the Pb scavengers 1,2 dichloroethane (EDC) and 1,2 dibromoethane (EDB) in sufficient quantities to give an atom ratio of Pb:Cl:Br of 1:2:1 (Associated Octel Ltd., 1981), and following combustion this mixture leads to emission of Pb from the exhaust, predominantly in the form of PbBrCl (Hirschler et al., 1957; Habibi, 1973). The proportion of Pb originally present in fuel which is emitted is dependent on factors such as engine speed and driving mode (Ter Haar et al., 1972; Habibi, 1973), but, over a period of time, only about 75% on average is emitted (Huntzicker et al., 1975). Some of the Pb not emitted is deposited in the engine, manifold and exhaust system, some retained in the engine oil and a small amount lost due to fuel evaporation (Laxen and Harrison, 1977).

Deposition of Pb at a particular location will be subject to many complex variables, including traffic density, driving mode, site topography and meteorological conditions (Baumann and Heumann, 1985). A particularly important factor will be the particle size distribution, and this appears to fall into two distinct size ranges; small

particles less than 1 μm in diameter, and large particles between 5 and 50 μm (Habibi, 1973; Ganley and Springer, 1974). The relative distribution between these two ranges is dependent upon driving mode and vehicle speed. Under cruise conditions, such as on a motorway, particles in the smaller size range will predominate, and Little and Wiffen (1978) reported that about 90% of the airborne Pb beside the M4 motorway was associated with particles less than 2 μm diameter. They also estimated that only about 20% of all Pb emitted at their M4 site was eventually deposited within 100 m of the carriageway, a result which they noted to be in accord with other studies. The remainder was assumed to have been dispersed by upward convection of the exhaust plume and prevailing winds, due to the extremely fine nature of the particles emitted. Ellis and Revitt (1982), however, in studies of the heavy metal content of road surface sediments, observed that for a motorway site, 62% of the total Pb content was associated with particle sizes between 100 and 500 μm, and suggested that Pb particulates were not present independently but were adsorbed onto larger particles. From a review of published data on road dust Pb content, the authors also noted that concentrations covered a wide range between 130 and 10000 $\mu g\ g^{-1}$.

The ease with which Pb and other heavy metals associated with road dust are removed from a motorway catchment during a runoff event is strongly dependent upon the different physico-chemical forms which the metals take (Laxen and Harrison, 1977). Speciation studies have been carried out using X-ray powder diffraction (XRD) by Olson and Skogerboe (1975) and Biggins and Harrison (1980), but although largely insoluble $PbSO_4$ was the major form of Pb detected by these means, the approach was limited by the small amount (about 1%) of Pb present in crystalline form amenable to XRD analysis. A technique of wider applicability is a sequential extraction procedure which examines the chemical associations of the metals present. A number of such procedures have been proposed in recent years for metals in soils and sediments (e.g. Tessier *et al.*, 1979; Salomons and Förstner, 1980; Förstner and Wittman, 1981). Harrison *et al.* (1981) and Hamilton *et al.* (1984) have used the scheme proposed by Tessier *et al.* (*op. cit.*) in studies of metal association in motorway and street dusts. The scheme allows the partitioning of Pb (and also Cd, Zn and Cu) into five fractions in order of relative ease of release of the metal, i.e.

the exchangeable, carbonate, Fe-Mn oxide, organic and residual phases; these terms are defined in Table 1.5. Both Harrison et al. (1981) and Hamilton et al. (1984) found that only a negligible proportion of the dust Pb content was in the exchangeable phase, and in general the two studies indicated that the Cd content was more easily extractable than either Pb or Zn, with data for Zn showing variable extractability between Pb and Cd. More recently speciation studies have been carried out on metals in runoff from a residential catchment (Morrison et al.; 1984) and runoff from the M6 in Lancashire (Harrison and Wilson, 1985a,b,c) and the results were in broad agreement with street dust studies.

TABLE 1.5 : Classification of trace metal fractions in sediments (after Tessier et al., 1979)

| Phase | Description |
|---|---|
| Exchangeable | Loosely bound metals; changes in ionic composition (e.g. due to de-icing) likely to affect sorption-desorption process. |
| Bound to Carbonates | Precipitates or co-precipitates susceptible to changes of pH; released by mild acid. |
| Bound to Fe-Mn oxides | Adsorbed or co-precipitated metals; thermo dynamically unstable and released under anoxic conditions. |
| Bound to Organic Matter | Complexed or adsorbed; released under oxidising conditions in natural waters. |
| Residual | Metal held within mineral lattices and not expected to be released in solution over a reasonable time under conditions normally encountered in nature. |

Polynuclear aromatic hydrocarbons (PAH) are widespread pollutants in urban atmospheres, and are mainly produced by high temperature reactions such as incomplete combustion and pyrolysis of fossil fuels and other organic materials. These compounds give rise to particular concern because of the strong carcinogenic and mutagenic activity of many of them (Haroz, 1983), and because the majority of airborne PAH are adsorbed on suspended particles within the respirable fraction, i.e. less than 5 μm diameter (Nikolaou et al., 1984). In urban areas sources will include emissions from vehicles, coal and oil-fired power stations, industrial processes, refuse burning and domestic heating appliances (Nikolaou et al., 1984), and in winter the contribution from heating sources may be considerably larger than that from vehicles (Harkov and Greenberg, 1985). In summer periods, however, vehicle emissions will predominate, and in the absence of other sources vehicle emissions will be the main source of PAH in a motorway catchment. This was demonstrated by Maoza (1979), who analysed soil samples in the vicinity of the M1 in Bedfordshire for PAH and found that concentrations of 7 PAH decreased rapidly, from about 3250 μg $kg^{-1}$ at the roadside to values of 20-30 μg $kg^{-1}$ at distances of 150-200 m. Similar striking trends were reported by Johnston and Harrison (1984) in studies of soils near the M6 motorway.

(ii) Leakage of Fuel, Lubricants, Hydraulic Fluids and Coolants

The loss of lubricants from moving vehicles is often sufficient to coat road surfaces with an organic layer which reduces the coefficient of friction between tyres and the road, clogs tyre treads and obscures road markings (Green, 1974). In addition, this is easily removed by surface runoff and has a high PAH load (Pope, 1980), while fuel, lubricants and hydraulic fluids lost to road surfaces have also been noted to degrade asphaltic surfaces and contribute to the inorganic solids loading which is removable in runoff (Sartor and Boyd, 1972). Lubricating oils contain Zn and Cd, where Zn is present in the form of stabilising additives such as zinc dithiophosphates, and Cd is present as an impurity in the original Zn used to prepare the additive (Lagerwerff and Specht, 1970). Some Pb retained in engine oil may also be deposited on the road surface as a result of oil leaks (Shaheen, 1975).

(iii) Emissions from Tyre, Clutch and Brake Linings

Dannis (1974) estimated that the average loss rate of rubber from a tyre was 90 mg $km^{-1}$, and on this basis calculated that the total tread lost per annum in the US was 720 x $10^6$ kg. The loss rate is influenced by factors such as vehicle speed, road surface condition, tye alignment and the amount of cornering. Under steady, straight line cruising conditions, the loss rate is generally lower (~30 mg $km^{-1}$) than on roads with many bends (Cadle and Williams, 1978). These authors also indicated that in general tyre wear particles are not suspendable and less than 5% of tyre wear products were airborne particulates. They noted that traces of gaseous pollutants such as hydrocarbons and sulphur compounds have been found to be emitted continuously under normal wear conditions, probably due to polymer pyrolysis at the tyre-road contact patch, but these emissions were found to be minimal compared with those from exhausts. Tyre wear products have also been cited as a source of PAH in road runoff (Harrison et al., 1975), and are a major potential source of Zn, since ZnO is used during tyre manufacture and tyre rubber contains in the region of 1% Zn (Christensen and Guinn, 1978). The use of PbO in tyre manufacture has also been noted (FHWA, 1981b). Cadmium may also be present in tyre rubber, again as a Zn-associated impurity (Lagerwerff and Specht, 1970).

Wear products from brake linings, disc pads and clutch facings may contribute not only to solids loadings on road surfaces but are also the main source of asbestos, and in addition some Cu may be deposited as a result of wear of Cu-impregnated brake linings (Shaheen, 1975). The FHWA (1981b) estimated that passenger cars, light trucks, medium trucks and heavy trucks produce in the region of 18, 55, 180 and 600 µg $km^{-1}$ asbestos respectively, with about 80% of wear products being deposited on the road surface.

(iv) Dirt, Dust, Decomposing Coatings, etc.

Loss of accumulated dirt, dust and rust deposits can be sources of solids and Fe on the road surface, while Ni and Cr, used in chrome plating for bumpers, etc., may also arise from these sources. Copper is also a common constituent of piping and other components (Harrop, 1983). Vibration or impact may lead to loss of glass and plastics as well as metals (Sartor and Boyd, 1972).

(v) Spillage of Vehicle Loads

Materials transported by road are subject to occasional spillage due to accident or negligence, and continuous in-transit losses may occur from uncovered loads of sand, gravel, etc., but those which are of the greatest concern for water quality are consignments of toxic or hazardous chemicals (Pope, 1980). In areas where major highways cross catchments forming a source of potable water supply, road drainage structures may include facilities to reduce the hazard from such occurrences (Floss and Sauer, 1978; Bosset, 1978; Adams, 1981). Due to their erratic and unpredictable nature, however, spillages are almost impossible to quantify in terms of volume or composition.

(b) Atmospheric Deposition

Atmospheric deposition can influence road surface runoff quality both through dry deposition between storm events and through the chemical quality of rainfall before it interacts with contaminants on the road surface. The extent to which these factors influence road runoff quality is the subject of considerable uncertainty, however, as Harrop (1983) revealed in his review of this topic. He noted that contributions from deposition can vary very widely both in composition and concentration, and this is also evident in the data reviewed by Pope (1980), summarised in Table 1.1. This variability is thought to arise largely because deposition quality, as with urban runoff itself, is greatly influenced by local and regional land use patterns and the proximity of anthropogenic emissions (Cawse, 1980; Munger and Eisenreich, 1983).

An attempt to assess the contribution of wet and dry deposition to surface runoff loadings in a specific catchment was made by Mance and Harman (1978) in their Stevenage study, and a summary of their results is given in Table 1.6. The data indicate that at this particular location the deposition contribution to runoff loads can be considerable for many parameters. In general, dry deposition (dustfall) and associated contaminants will be expected to make a smaller contribution to motorway surface runoff in a rural area, as indicated by the data from Goettle and Krauth (1980) given in Table 1.7. An assessment of the contribution of this particular source to runoff quality at a specific location appears to require simultaneous

sampling of deposition quality where possible.

TABLE 1.6 : Percentage contribution of atmospheric deposition to urban surface runoff (after Mance and Harman, 1978)

| Parameters | Percentage |
|---|---|
| Suspended solids | 23 |
| Dissolved solids | 30 |
| Total solids | 29 |
| Chloride | 28 |
| Zinc | 38 |
| Lead | 54 |
| Copper | 96 |
| Manganese | 49 |

TABLE 1.7 : Dustfall rates for different land use types (after Goettle and Krauth (1980) and references therein)

| Land Use Type | Rate of Dustfall ($g\ m^{-2}\ month^{-1}$) |
|---|---|
| Rural areas | 2.5-3.3 |
| Urban areas | 3.3-6.3 |
| Large urban areas | 5.5-6.0 |
| Industrial areas | 10-60 |

(c) De-icing Activities

Sodium chloride in the form of rock salt is the most widely used material for de-icing of roads and motorways in many countries, including the UK, and its advantages are its efficiency in melting snow and ice, short application time and low costs of application (Field et al., 1974). Nonetheless, its widespread use in recent decades has led to a number of adverse environmental effects, which were reviewed by Field et al. (1974) and Crowley (1981), and which include ground and surface water (including sources of potable supply), pollution damage to motorway structures and concrete road surfaces, vehicular corrosion and damage to roadside soils, vegetation and trees. Many cases of contamination by de-icing salt of groundwater sources or

potable supply have been reported in the USA (Crowley, 1981), while in the UK adverse affects on supplies have been recorded in some locations. De-icing salt in runoff from the M1 in Northamptonshire contaminated a nearby reservoir to such an extent that extensive modification of the treatment works was required to reduce hardness (Seddon, 1975). Other instances of reservoir contamination by de-icing salt in M1 runoff have also been reported (Crowley, 1981; Rose, 1984).

The rate of application in the UK as recommended by the Department of the Environment is between 14 and 56 $gm^{-2}$, depending on weather conditions, but in practice the actual rate is set by drivers of gritting vehicles after a visual examination of the prevailing conditions (Hedley and Lockley, 1975). Motorway interchanges used by different highway authorities for access to adjoining stretches of motorway may receive multiple applications of salt, and in some areas of the UK de-icing salt is suspected of causing increased rates of breakdown of bitumen surfaces (Williamson, 1968).

In addition to the effects of sodium chloride itself, de-icing salt also contains potassium or sodium ferrocyanides, added as an anti-caking agent at concentrations of about 100 ppm, and a wide range of trace impurities (Hedley and Lockley, 1975; Imperial Chemical Industries Ltd., 1983), as shown in Table 1.8. Ferrocyanide presence has caused concern in the past, due to its photochemical breakdown to form cyanide (Crowley, 1981). Although in general the concentrations of other trace impurities are low (Table 1.8), the amounts of salt applied to motorways may mean that receiving water concentrations may remain significant in environmental terms despite the effects of dilution, and the effects of this in the case of bromide are discussed in section 1.2 following. An indirect effect of de-icing salt has been noted by Feick et al. (1972), who observed increased mobilisation of mercury from stream bottom sediments in the presence of high sodium chloride concentrations due to complexation of $Hg^{+}$ with $CL^{-}$ and competition between $Na^{+}$ and $Hg^{+}$ for exchange sites on sediments. Förstner and Wittman (1981) have also suggested that a similar mechanism may be responsible for $Pb^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ release from sediments at elevated salt concentrations. Such effects were predicted by Hahne and Kroontje (173) from theoretical considerations of complexation

TABLE 1.8 : Typical composition data for de-icing salt used in the UK

| ICI Ltd. (1983) | | | Hedley and Lockley (1975) | |
|---|---|---|---|---|
| Constituent | Concentration (% or ppm w/w) | | Constituent | Concentration (% or ppm w/w) |
| | Soluble Fraction | Insoluble Fraction[a] | | |
| NaCl | 92.7% | - | NaCl | 90.6% |
| $SO_4^{2-}$ | 1.4% | 12.7% | SS | 9.2% |
| $CO_3^{2-}$ | - | 14.6% | Fe | 0.16% |
| $Fe(CN)_6^{4-}$ | 100 ppm | - | Ni | 12 ppm |
| $Fe(CN)_6^{3}$ | <10 ppm | - | Pb | 8.7 ppm |
| $Br^-$ | 220 ppm | - | Zn | 6 ppm |
| $SiO_2$ | 70 ppm | 42.9% | Cr | 4.7 ppm |
| Ca | 0.55% | 6.6% | Cyanide | 5.7 ppm |
| Mg | 290 ppm | 5.0% | | |
| Sr | 110 ppm | 320 ppm | | |
| Cr | <1 ppm | 80 ppm | | |
| Al | <3 ppm | 5.4% | | |
| Ba | 10 ppm | 350 ppm | | |
| V | <7 ppm | <100 ppm | | |
| Cd | 0.4 ppm | <6 ppm | | |
| Pb | <3 ppm | <50 ppm | | |
| Fe | 26 ppm | 3.1% | | |
| Zn | 4 ppm | 130 ppm | | |
| Mn | 0.4 ppm | 670 ppm | | |
| Cu | <2 ppm | 240 ppm | | |
| K | 120 ppm | 2.8 ppm | | |
| Ti | <20 ppm | 0.6% | | |

[a] = % Insolubles : 5.2%

reactions of Zn, Cd and Hg with $Cl^-$. At present, research is underway in the US to assess an alternative de-icing agent, calcium magnesium acetate, which it is hoped will alleviate some of the environmental effects of sodium chloride (Chollar, 1984).

(d) Road Surface Erosion

Road surfaces are themselves sources of solids which accumulate on them, due principally to wear. The type of material used to construct the road surface has been found to have a substantial influence on the surface solids loading (Sartor and Boyd, 1972). These authors concluded that asphalt road surfaces had in the region of 80% greater total solids loadings compared with concrete surfaces. In addition, road surface condition is also an important factor, and Sartor and Boyd (op. cit.) also noted that roads in fair to poor condition gave rise to total solids loading in the region of 2.5 times greater than roads in good to excellent condition. Road surface markings may contribute a small amount of Pb to runoff loadings when yellow lines, containing lead chromate, are abraded (Harrop, 1983), while Ellis et al. (1981) have noted the occurrence of a peak in titanium concentrations late in a storm flow, and also attributed this to degradation of road surface markings. Bituminuous road surfaces have also been cited as a source of PAH in road runoff (Harrison et al., 1975).

1.1.3 Contaminant Removal and Runoff Quality Modelling

Contaminants accumulated on a road surface may be removed by one or more of the following mechanisms (Bellinger et al., 1982):

(i) Soluble contaminants dissolving in runoff prior to subsequent removal.

(ii) Insoluble particulates and associated contaminants transported by runoff, which may be considered essentially as sediment transport.

(iii) Removal by air dispersal, involving transfer of the surface contaminants to the atmosphere either as dry, discrete particles or dissolved in surface spray water.

(iv) Removal by road cleaning practices.

Waterborne removal of contaminants in spray from mechanism (iii) has not been widely studied, and reported data are either inconclusive (Bellinger et al., 1982) or indicate a limited role (Bufill, 1981). Consideration will thus be confined to mechanisms (i) and (ii) which result in direct discharge to receiving waters.

Sartor and Boyd (1972) observed that the rate at which material was removed from a road surface by rainfall was largely dependent on rainfall intensity and road surface characteristics, and Bellinger et al. (op. cit.) noted that several workers had used an exponential relationship between surface loading and rainfall to describe the removal of surface contaminants during individual events:

$$Li - Lr = Li(1-\exp(-KR))$$

where $Li$ = initial surface loading (mg $m^{-2}$)

$Lr$ = surface loading after time t (mg $m^{-2}$)

$R$ = cumulative rainfall (actual or effective) up to time t

$K$ = removal constant ($mm^{-1}$), which reflects the ease of removal of a particular contaminant and is thus contaminant dependent

Values of K for various contaminants noted by Laxen and Harrison (1977) ranged from 1.8 $mm^{-1}$ for sodium from de-icing salt to 0.1 $mm^{-1}$ for suspended solids, the higher value for sodium reflecting its higher solubility and greater ease of removal. Alley and Smith (1981) have proposed an optimisation technique for determining the best fit value for K for a series of storm events, while Wada and Miura (1984) have recently suggested a more sophisticated approach which allows for street cleaning at varying intervals. In general, however, such approaches are best suited for easily removed soluble components, and the complexity of suspended solids transport in runoff still lacks an adequate modelling approach (Harrison and Wilson, 1985a).

Apart from single event modelling, a number of workers have attmepted to utilise the advantages of well-defined motorway catchments to analyse factors affecting final outfall contaminant loadings

on a statistical basis (Cathelain et al., 1981; Asplund et al., 1982; Chui et al., 1982; Balades et al., 1984). These authors reported that the following variables were found to influence runoff loadings;

(i) volume of runoff

(ii) duration of runoff

(iii) duration of rainfall

(iv) maximum rainfall intensity

(v) total rainfall

(vi) length of time elapsing between start of storm and beginning of runoff

(vii) duration of preceding dry period

(viii) dry period traffic flow

(ix) in-storm traffic flow

Considerable variability exists, however, between the studies in terms of the degree of influence which each of these factors was found to have on runoff quality. Asplund et al. (op. cit.), for instance, concluded that in-storm traffic flow has a major influence on suspended solids loads, while Balades et al. (op. cit.) stated that no clear relationship between traffic flows and contaminant loads was apparent. Both Cathelain et al. (op. cit.) and Balades et al. found, however, that flow-related parameters, such as volume of runoff and peak rainfall intensity, influenced loadings to a considerable extent.

Runoff quality data obtained from five highway catchments during the FHWA (1981a) study were utilised to construct a predictive model for highway runoff pollutant loadings (FHWA, 1981c). Extensive statistical analysis of factors affecting runoff quality was not attempted, but field data were used to find the optimum values for coefficients in a model using an exponential-type removal (as previously discussed) and assuming linear accumulation of contaminants on road surfaces with time. In general, long term cumulative loadings

over many events (summer only) were found to fall within ±30% of observed values (except for a site with extended dry periods), although individual event loads were not well predicted. Nonetheless, such an approach suggests that modelling of long term loadings may be a useful objective and need not require a detailed understanding of all the possible factors involved.

## 1.2 Bromide in Motorway and Road Runoff

### 1.2.1 Reasons for Concern

There has been considerable speculation in developed countries in recent years that trace organic chemicals in potable water supplies may play a role in initiating illnesses such as cancer (Kool et al., 1982). In particular, great concern has arisen over the production of trihalomethanes (THM) during chlorination, following studies by Kleopfer and Fairless (1972) and Rook (1974) which demonstrated the presence of chlorinated and brominated volatile organic species in drinking water, especially chloroform. These reports concluded that THM were formed during the chlorination stage of water treatment, through the reaction of chlorine with naturally coloured water. Subsequent surveys in several countries (Symons et al., 1975; Foley and Massingham, 1976; Luong et al., 1980) confirmed that THM are commonly found in waters treated with chlorine, with chloroform concentrations ranging from $<1\ \mu g l^{-1}$ to over $100\ \mu g l^{-1}$. Bull (1982), in a review of the THM toxicological research situation in the US, noted that concern about chloroform arose from reports that it is carcinogenic in both mice and rats, and that chloroform had received most attention in toxicological studies. In contrast, studies of the other three most commonly occurring THM (bromoform, dibromochloromethane and dichlorobromomethane) were only at an initial stage. In the pure form, however, brominated haloforms are more toxic than chloroform (Irving Sax, 1979), and recent reports now indicate a greater toxicity of these compounds to cell cultures than chloroform (Mochida and Yamasaki,1984).

The frequent occurrence of brominated THM has aroused specific interest, since bromide ($Br^-$*) is usually present in source waters during chlorination in concentrations far lower than those of chlorine ($Cl_2$) or chloride ($Cl^-$*) with a typical Cl/Br concentration ratio range being 29-138 (Prest, 1982). During chlorination, however, both HOBr and HOCl are present in solution (HOBr being present due to $Br^-$ oxidation by $Cl_2$), but HOBr reacts more selectively and rapidly than HOCl with the organic precursors which lead to THM formation (Rook et al., 1978). This leads to a greater fraction of brominated THM compounds being produced than reflected by the original Cl/Br ratio in the treated water. Thus upland waters containing low natural $Br^-$ levels will be expected to produce a lower fraction of brominated THM than a lowland water with higher $Br^-$ concentrations, and this expectation was confirmed in studies by Luong et al. (1980; 1982). Thus the $Br^-$ content of source waters is an important factor in determining final THM composition, and its importance in THM formation when present at very low concentrations (50 $\mu g\ l^{-1}$ or less) has greatly increased awareness of $Br^-$ as an important water quality parameter (Haag et al., 1984).

When anthropogenic sources of $Br^-$ are absent, the main potential sources in surface waters appear to be those of a geochemical or marine background origin, and reported concentrations are generally low, e.g. $10\mu gl^{-1}$ (Vinogradov, 1959), $14\mu gl^{-1}$ (Bowen, 1979), 30-280 $\mu gl^{-1}$ (Masschelein and Dennis, 1981), 75-171 $\mu gl^{-1}$ (Pyen et al., 1980) and 59 $\mu g\ l^{-1}$ (Habib and Minski, 1981). Non-natural sources may include point source industrial discharges and sewage works effluents (Luong et al., 1983) and fumigation of soils and crops with methyl bromide (Cooper et al., 1985), but the source of particular relevance to motorway runoff studies is the previously noted widespread use of EDB as a scavenger for Pb in petrol. From the studies of highway runoff discussed previously, it is clear that Pb is one of the most significant characteristic constituents of this type of sample, and since, therefore, in the absence of specific industrial

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* The chemical symbols '$Br^-$' and '$Cl^-$' will be used in this work to indicate 'bromide' and 'chloride' in all references to aqueous media. Use in other media will be noted where appropriate.

sources, the dominant contributor of this element is vehicle exhaust, it is to be expected that this could also be a major source of $Br^-$ in road runoff. Deicing salt has also been shown to have a $Br^-$ content in the region of 220 mg $kg^{-1}$ (Table 1.8), and must therefore also be considered a potential additional source in areas where significant amounts of de-icing salt are applied in winter months.

### 1.2.2 Potential Sources of Bromide in Motorway and Road Runoff

#### (a) Vehicle Emissions

As noted in section 1.1.2(a), the combination of TAL compounds and EDB together in petrol to give a Pb:Cl:Br atom ratio of 1:2:1 leads to the majority of Pb being emitted in the form of lead bromochloride, PbBrCl, and early studies by Winchester *et al.* (1967) in Fairbanks, Alaska, Martens *et al.* (1973) in San Francisco and Moyers *et al.* (1972) in Cambridge, Mass, confirmed a close association between atmospheric particulate Pb and bromine (Br)* in the absence of industrial sources of these elements. In Perth, Australia, O'Connor *et al.* (1977) found that the bromine/lead (Br/Pb) ratio in atmospheric particulates was close enough to that in petrol to suggest the use of this ratio and atmospheric Br levels to estimate atmospheric Pb concentrations. Clearly, therefore, vehicle exhaust must also be regarded as a potential source of $Br^-$ as well as Pb in road runoff, and a recent comprehensive review by Harrison and Sturges (1983a) of published work on Br/Pb ratios found in urban centres in many parts of the world confirmed the ubiquity of elevated atmospheric Br levels comparable with Pb concentrations where high traffic flows prevail. A selection typical of values presented is given in Table 1.9.

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* Following general convention in the literature, the symbols 'Br' and 'Cl' will be used to denote the words 'bromine' and 'chlorine' when used with respect to atmospheric and other non-aqueous media. Since the precise chemical form of the bromine and chlorine referred to is often not stated or not known, however, the use of these symbols does not refer to a specific chemical state, except where otherwise indicated.

TABLE 1.9 : Typical literature values for Br and Pb concentrations and Br/Pb ratios in urban air (after Harrison and Sturges, 1983a)

| Sampling Location | Type of Site | Br[a] concn ($\mu gm^{-3}$) | Pb[a] concn ($\mu gm^{-3}$) | Br/Pb[a] | Sampling Duration | Reference |
|---|---|---|---|---|---|---|
| San Francisco Bay | Nr freeway | 0.28[b] | 0.80[b] | 0.35[b] | 96 h | Martens et al. (1973) |
| | Others | 0.06-0.46 | 0.32-1.58 | 0.18-0.29 | " | |
| Birmingham, UK | City kerb | 1.12 | 2.41 | 0.34 | 1 day | McKee et al. (1980) |
| | University campus | 0.34 | 0.98 | 0.24 | | |
| Fairbanks, Alaska | Downtown | 0.46 | 3.68 | 0.15 | few hours | Winchester et al. (1967) |
| Los Angeles[c] | Freeway | 0.5-7.0 | 1.0-15 | 0.32-0.45 | 2 h | Giauque et al. (1974) |
| Toronto | City centre | 0.28 | 0.97 | 0.29 | 24 h | Paciga et al. (1975) |
| | Freeway (100 m) | 0.34 | 1.02 | 0.33 | " | |
| Los Angeles[d] | Freeway | 4.9 | 10.9 | 0.47 | ~4 h | Dzubay et al. (1979) |
| | "Background" | 0.6 | 1.7 | 0.33 | " | |
| Lancaster, uK[e] | Town centre | 0.10-0.40 | 0.32-1.13 | 0.33-0.37 | 3 h | Harrison & Sturges (1983b) |

a = mean values except where indicated
b = single value
c = particles $<0.5$ µm, smog episode
d = particles $<2.4$ µm
e = particles $<1.5$ µm

Although the predominance of PbBrCl as the main particulate form of Br in exhaust gas and ambient air is well established, very little information exists on the ultimate fate of the Br content itself. Concern over the health effects of airborne Pb has meant that analysis of Br in air has almost always been undertaken in order to relate the Br/Pb air ratio to the Br/Pb ratio in petrol (0.39, henceforth termed the "ethyl ratio") as a means of clearly identifying vehicle emissions as a major source of airborne Pb (O'Connor et al., 1977). Major non-vehicular sources of Br in air are not common (Patty, 1963) and Br and Pb concentrations are thus generally closely related.

With respect to the fate of vehicle-derived Br, however, a major feature of interest in the studies reviewed by Harrison and Sturges (1983a) was that many atmospheric Br/Pb values reported from a wide variety of urban and suburban sites using various sampling techniques were less than the ethyl ratio and, as a rule, samples from rural or suburban sites tended to show lower Br/Pb ratios than those in busy urban or freeway locations. In the absence of non-vehicular Pb sources, this effect was generally acknowledged as being due to an ageing process involving Br loss whose precise mechanism is as yet imperfectly understood. Particulate Pb samples from non-urban areas will generally have travelled further from their point of origin, aged more and thus have a lower Br/Pb ratio.

Since, however, this effect can reduce the usefulness of Br/Pb ratio studies in identifying sources of Pb emissions, several studies have been undertaken to investigate the mechanisms of Br loss, and a variety of processes have been proposed i.e. oxidation of bromide ion by atmospheric oxidants (Loucks and Winchester, 1970), replacement of bromide and chloride ions by acid-base type reactions with carbonate and hydroxide ions (Ter Haar and Bayard, 1971) and photochemical reactions (Pierrard, 1969; Boyer and Laitinen (1974), but at present the work of Biggins and Harrison (1979) on the atmospheric chemistry of vehicular Pb aerosols appears to give the most satisfactory account available for the occurrence of many Pb compounds found in aged aerosols.

The mechanisms which they proposed to account for these compounds, such as $PbSO_4$ and $2PbBrCl.NH_4Br$, were based on experimental work investigating the reactions of fresh exhaust-generated PbBrCl with artificial atmospheres containing various commonly encountered air pollutants. The only reactions of PbBrCl which led to halogen loss (as HBr and HCl) were with mists of 1M sulphuric acid and 1M $NH_4HSO_4$:

$$PbBrCl + H_2SO_4 \rightarrow PbSO_4 + HBr + HCl \quad (1)$$

$$6PbBrCl + 2NH_4HSO_4 \rightarrow 2PbSO_4 + 2PbBrCl.NH_4Br + \alpha - 2PbBrCl.NH_4Cl + HCl + HBr \quad (2)$$

These are abundant in polluted atmospheres, and being hygroscopic will exist as very fine aqueous solution droplets in the relatively humid conditions prevalent in the UK. Fine exhaust particles will tend to coagulate rapidly with these droplets if present in large numbers, and, in theory, react with the sulphates to lose halogens within a short period of time.

This mechanism was held to explain the enhanced Br loss frequently observed in summer (e.g. O'Connor et al., 1977; Rentschler and Schreiber, 1977) by more intense photochemical oxidation of $SO_2$ leading to greater levels of $H_2SO_4$ and $NH_4HSO_4$ relative to other pollutants, while the presence of $PbSO_4$ in road dusts (Olson and Skogerboe, 1975) would also be accounted for. In the context of the contribution to road runoff $Br^-$ sources, however, even more relevant is the fact that this theory predicts loss of Br as highly soluble HBr, which would clearly be easily removed from the atmosphere by rainfall and contribute to runoff $Br^-$ loadings. In addition, road surfaces are generally basic in nature (Harrison and Wilson, 1985a) and it appears possible that HBr could be adsorbed on such surfaces during dry periods, followed by rapid solubilisation and removal in runoff during storm events.

Although loss of Br from exhaust particulates in ambient air appears to be a major potential source of $Br^-$ in road surface runoff, a number of the studies reviewed by Harrison and Sturges (1983a) reported Br/Pb values equal to or higher than the ethyl ratio, with

values ranging from 0.4 (Pierson and Brachaczek, 1976) to 0.55 (Hollowell et al., 1977), while more recently Bullin et al. (1985) have reported values of up to 0.58 in particulates near a Texas intersection. Such results indicate that the Br loss mechanism may not be as widespread or rapid a phenomenon as anticipated, and an important common factor in the studies quoted was that sampling took place close to major highways, which suggests that Br loss does not always occur sufficiently rapidly to cause any significant difference between sampled ambient air Br/Pb ratios and the ethyl ratio.

Values of the Br/Pb ratio greater than 0.39 also suggest that preferential emission of Br from the exhaust system leading to subsequent filter retention can take place in some circumstances (Harrison and Sturges, 1983a). This appears to be a reasonable explanation, in view of the widely recognised retention within vehicle engines and exhaust systems of some 20-30% of fuel Pb content over time (Huntzicker et al., 1975). Although the majority of Pb actually emitted is in the form of PbBrCl (Br/Pb 0.39), the question as to the fate of the excess Br remains. From the published work available on this topic, the most likely routes for Pb-independent Br emissions appear to be:

(i) in volatile organic form, such as EDB or methyl bromide

(ii) in inorganic form, either as $NH_4Br$ or HBr.

Item (i) is not generally considered significant in terms of the filter retention under consideration here (Baumann and Heumann, 1985) but will be considered shortly as an additional potential source of Br in road runoff. Item (ii) was the subject of a dynamometer-based exhaust gas study by Li and Smith (1976), using a typical saloon car running on standard fuel under 40 and 50 mph cruise conditions. Filters and gas scrubbers were used to trap particulate and non-particulate exhaust products. They concluded that, apart from PbBrCl, particulate $NH_4Br$ was the other major inorganic form of exhaust Br, with HBr being negligible initially. Post-emission formation of HBr was considered probable, however, arising from the equilibrium reaction:

$$NH_4Br \rightleftharpoons HBr + NH_3 \qquad (3)$$

Of the Br and Pb initially present in the fuel, a considerably greater proportion of the Br was emitted than of Pb, leading to overall Br/Pb ratios of between 1.0 and 3.9, although how these high values would relate to those found under long-term working conditions was not considered. Nonetheless the study appears to indicate clearly that emission of Br in the form of $NH_4Br$ can take place, and retention of this on sampling filters would subsequently lead to Br/Pb ratio greater than 0.39 being detected. Moreover, this form of atmospheric Br would also be readily water-soluble and removeable in runoff, although, as Harrison and Sturges noted (1983a), many details of the atmospheric chemistry of $NH_4Br$ and HBr are still unclear.

In addition to inorganic forms of Br, the detection of volatile organic forms of Br in exhaust gases and ambient air by several workers raises the possibility that these forms are also potential sources of vehicle-derived Br in runoff. Methyl bromide in exhaust gas (71-217 $\mu g\ m^{-3}$) and ambient air ($<$0.04-0.87 $\mu g\ m^{-3}$) was reported by Harsch and Rasmussen (1977), and EDB concentrations in urban air varying between 0.001 and 1.26 $\mu g\ m^{-3}$ have been reported by Leinster *et al.* (1978) and Tsani-Bazaca *et al.* (1981). The presence of EDB was attributed to evaporative losses from fuel tanks and exhaust emissions (Leinster *et al.*, 1978). Clark *et al.* (1984) also monitored EDB concentrations from a site beside the M1 in Bedforshire and found a mean concentration of 0.36 $\mu g\ m^{-3}$, which fell within the range of many particulate Br concentrations at highway sites reported by Harrison and Sturges (Table 1.9). Such results indicate that volatile organic forms of Br may also be potential sources of runoff $Br^-$, although the processes which may occur between emission of such compounds and their eventual removal in runoff have received no in-depth study.

Apart from airborne sources of $Br^-$ in runoff, an additional potential source is the leaching of $Br^-$ from deposited PbBrCl particulates. As with many aspects of vehicle-derived Br, however, this topic has also received very little study. Boggess and Wixson (1979), however, presented data from laboratory solubility studies of synthetic PbBrCl, showing that solubilities ranged from 4.38 $gl^{-1}$ at 0°C to 9.55 $gl^{-1}$ at 40°C. From the data obtained, thermodynamic considerations led to the conclusion that PbBrCl was the stable solid

phase, rather than $PbBr_2$ or $PbCl_2$, and they suggested a solubilisation reaction of the form

$$PbBrCl \rightleftarrows Pb^{2+} + Br^- + Cl^-$$

Abdullah and Royle (1973), cited by Demayo et al. (1982), suggested that $PbCl^+$ may also be present in pure solution. Such studies may, however, be of limited value in assessing the behaviour of exhaust-derived PbBrCl in a polluted aqueous environment such as road runoff, but no direct studies appear to have been reported. Indirect evidence for $Br^-$ leaching was, however, derived from measurements of the Br and Pb content of Glasgow street dusts by Farmer and Cross (1979), who found a range of Br/Pb values between 0.02 and 0.08, and concluded that such low values compared with normal air values indicated a combination of gaseous Br loss and leaching following deposition. Hopke et al. (1980) also reported a low Br/Pb ratio of 0.08 in a bulk sample of street dust from Urbana, Illinois, and Bullin and Moe (1982) reported a value of 0.17 in a sample of Texas roadside dust, but no details were given in either case. Nonetheless, these data indicate clearly that even if little or no loss of Br occurs from PbBrCl in ambient air before deposition, Br is still largely lost from such particulates following the processes of agglomeration, deposition and contact with runoff water, and this will almost certainly contribute to final $Br^-$ levels in runoff.

In summary, therefore, the available literature indicates that vehicle-derived Br in a motorway catchment may be present in the form of PbBrCl, HBr, $NH_4Br$ or volatile organic compounds. The behaviour of the organic forms with respect to surface runoff is not clear, but the remaining inorganic forms are clearly all capable of making a contribution to ultimate $Br^-$ concentrations.

(b) De-icing Salt

De-icing salt was identified in section 1.1.2(c) previously as having a major impact on motorway runoff quality during winter months, and Table 1.8 presented data for a range of impurities in salt which may contribute to receiving water concentrations. From the table it is evident that, apart from suspended solids and major ions, $Br^-$ is one

of the most abundant trace impurities, being present in concentrations in the region of 220 ppm. Thus de-icing salt must be considered an additional potential source of $Br^-$ in motorway runoff waters during periods of de-icing activity, especially as $Br^-$ in de-icing salt is almost entirely in soluble form. No detailed studies of this topic appear to have been carried out however, apart from the work of Sollars et al. (1982), but this was based on data presented in section 6 of the present work and is discussed therein. Comparison of $Cl^-$ and $Br^-$ de-icing salt contents in Table 1.8 (ICI data) shows, however, that 1 $mgl^{-1}$ of salt-derived $Cl^-$ in runoff water would be accompanied by a $Br^-$ concentration of 0.4 $\mu gl^{-1}$. Application of this ratio to the maximum $Cl^-$ concentrations given in Table 1.3 from the studies by Hedley and Lockley (23670 $mgl^{-1}$) and the FHWA (13300 $mgl^{-1}$) suggests that accompanying $Br^-$ concentrations (assuming non-salt $Cl^-$ concentration is minimal) could have been in the region of 9.5 and 5.3 $mgl^{-1}$ respectively. Such concentrations are clearly far in excess of those found to produce brominated THM formation during chlorination (Luong et al., 1982) and would require con siderable dilution before falling below those levels.

(c) Background Sources

The chief background (i.e. not road-related) sources of $Br^-$ in motorway runoff from a catchment which does not receive drainage from other areas will be mainly derived from atmospheric deposition, while in other cases runoff from adjacent areas may make an additional contribution. In general, however, reported concentrations in atmospheric (wet) deposition in areas away from major roads is generally very low e.g. 17 $\mu gl^{-1}$ (Cawse and Pierson, 1972); 28 $\mu gl^{-1}$ (Slanina et al., 1979) and this is therefore probably not a major contributor to runoff loads in most cases. Runoff from verges or other pervious areas treated with Br-containing herbicides or insecticides such as 'Bromacil' and 'Bromofenoxin' (British Crop Protection Council, 1979) may make an additional contribution in some locations, but the extent of use of such compounds on verges etc. is not documented and no studies on this aspect of road runoff have been reported.

In conclusion, therefore, it is clear that the $Br^-$ content of motorway and road runoff has received very little attention to date,

but the available evidence suggests clearly that vehicle emissions and de-icing salt will be the main sources of $Br^-$ in runoff in most areas.

## 1.3 Treatment of Motorway Runoff

The accumulating evidence of the poor quality of highway runoff has led to increasing attention being paid to on-site treatment for major roads in rural areas, especially those crossing areas which form part of a potable water supply catchment. In specific locations where accidental spillage of chemicals from tankers may cause a major immediate hazard to surface or groundwater sources, holding tanks or other precautions may be installed as part of the highway drainage system (Floss and Sauer, 1978; Bosset, 1978; Adams, 1981). More generally, however, widespread installation of any form of advanced treatment for motorway runoff is ruled out on the grounds both of capital and maintenance costs. Treatment systems adopted for this specific problem must therefore be simple, low cost and, as far as possible, maintenance-free.

A survey of the available literature reveals that very little work has been done on assessing the effectiveness of treatment methods specifically adopted for motorway runoff treatment. A 1978 OECD conference considered various aspects of the impact of highway drainage on the environment. Of the eleven papers presented on this topic, only one author, Borch-Jensen (1978) presented specific data for a road runoff treatment system. The effectiveness of a settlement lagoon (minimum volume and depth 300 $m^3$ and 40 cm respectively) was evaluated for the treatment of runoff from a section of a Danish rural highway and surrounding verge of impermeable area 1.8 ha and permeable area 2.1 ha respectively. Over three storm events, mean reductions in effluent concentrations of suspended solids, lead and COD were 98, 95 and 69% respectively. Effluent concentrations were below government guideline limits for effluent to lakes and streams, and the results considered sufficiently encouraging to warrant further investigation. From other conference contributions, it appears that settlement ponds (with or without oil separators) are one of the more widely used treatment methods adopted in European countries. In Switzerland, for example, motorway drainage systems must, by law, incorporate oil separators (Heirli, 1978). No detailed studies on the efficiency of

these was reported, however. In the UK, Bellinger et al. (1982) reported that oil separators were in use to prevent pollution of a leisure lake by runoff from a service area on the M6 in Lancashire, but no details were given.

French drains have been utilised in some locations for a number of years as a means of draining motorway runoff from carriageways in Britain (Bartlett, 1981) and elsewhere, but their effect on runoff quality appears to have received very little in-depth study, apart from a brief account by Cathelain et al. (1981). The authors studied the effects of passing runoff through a "percolating filter", consisting of a 25 cm depth of small stones over 25 cms of fine gravel, with a 50 cm layer of sand on top. Over 15 events, concentrations of COD, BOD, TSS, Zn and Pb between inlet and outlet were reduced by 63, 52, 84, 66 and 85% respectively, although the variability in all these figures was high, due to periodic blocking of the filter, which was found to occur about once every two months. No detailed measurements were given, but from an illustration the gravel area appeared to be approximately 4 m x 68 m, taking runoff from 5735 $m^2$ of motorway.

Apart from locations where french drains are installed, gully pots and conduits are the other most widespread means of removing surface runoff from motorways in the UK, but no comparative data for their effect on runoff quality in such locations is available. A few studies of gully pot liquor quality have been carried out in UK urban areas, however, and these were reviewed by Harrop (1983). He noted that, in general, liquors were found to become anoxic within 24 hours of a storm event, and, rather than reduce contaminant levels in effluent, frequently added to those contributed during storm events themselves. Typical figures for gully pot liquor contribution to stormwater pollutant loads for suspended solids, dissolved solids, COD and BOD were 10.6, 20.7, 20.5 and 13.9% respectively. No detailed studies on long-term gully pot sediment removal efficiencies have been reported, but Ellis and Harrop (1983) observed that the mean size of basal sediments fell between 1000 and 2000μm, with only 5% less than 60 μm. These results were in general agreement with those of Pratt and Adams (1984), and indicate clearly that only large, easily settleable solids are easily removed, although it is fine sediment in road surface dusts which has frequently been observed to carry the

highest concentrations of associated contaminants, such as heavy metals (Harrison et al., 1981; Ellis and Revitt, 1982).

From the literature available, therefore, it is clear that although basic treatment of motorway runoff is undertaken in a number of countries, almost no comprehensive data exist on the effectiveness of these methods, and that more research is necessary to establish the basic characteristics and long-term suitability of the options available.

## 1.4 Objectives of Study

In the context of the preceding discussion, the objectives of the present work were defined as follows:

(a) Evaluation of the water quality of runoff from a motorway catchment in terms of a number of water quality parameters and their relationship to a range of hydrological and environmental factors.

(b) Evaluation of a suitable analytical technique for $Br^-$ in runoff and other samples.

(c) Identification of the sources of $Br^-$ and Pb in the catchment area.

(d) Examination of the concentrations and loads of $Br^-$ and Pb to be found in runoff from the catchment area, their relationship to each other, to other quality parameters and to hydrological and traffic variables.

(e) To carry out a preliminary examination of the effectiveness of a french drain and a sedimentation tank as methods of treatment of motorway runoff.

## SECTION 2. MOTORWAY SITE CONSTRUCTION AND SAMPLING METHODS

### 2.1 The Motorway Catchment

#### 2.1.1 Background to Site Selection

Investigations into the quality of motorway runoff at Imperial College were first undertaken in 1972, when a pilot study was carried out using a catchment on the M4 having a compound drainage system, in order to assess the suitability of such a catchment for runoff quality.

The advantages of such a catchment were considered to be as follows:

(i) The longer the length of road, the more surface area for component deposition, and thus the greater the quantities to measure.

(ii) The greater the surface area, the greater the volume of water to be dealt with, thus allowing the use of cheaper, less sensitive larger range equipment, which is easier to install and maintain.

(iii) Where a compound drainage system falls out into surface water, it would be possible to directly monitor the impact of the road runoff on water quality indices.

It was soon discovered, however, that such an approach builds in many sources of uncertainty when attempting to relate final quality with hydrological and traffic flow conditions. These problems are:

(a) Drainage systems, no matter how short, are contributing agents to the variability of the quality of water running through them. Thus, with motorway drains, materials will be adsorbed and released from inner pipe surfaces. There is also a potential for leakages, permitting losses from, or additions to, the road surface water, depending on hydrological conditions.

(b) The conduits themselves often provide sinks for the retention of sediments and associated compounds. These may subsequently be released under atypical conditions, such as infrequent, high intensity events, or they may undergo chemical change during retention.

(c) A catchment of large surface area, even when consisting entirely of motorway surface, has more hydraulic irregularities than a small one, e.g. changes in slope, surface texture or porosity. Changes in slope are a particular feature of curved sections of motorway, and are undesirable because a three-dimensional surface (catchment plus drainage) does not necessarily function in a constant manner over a range of hydraulic conditions. Precise definition of the catchment areas is also rendered more difficult.

To overcome these problems, a relatively simple, two-dimensional surface is required which provides, as far as possible, hydraulic and hydrological uniformity and which requires the absolute minimum of conduit lengths between the lowest point of the catchment and the sampling point. Such a catchment was identified in 1976 on a length of the southbound carriageway of the M1 motorway, between Toddington Motorway Services and Junction 11, about 56 km north west of London. Assistance in choosing the precise location was rendered by the Institute of Hydrology and the Transport and Road Research Laboratory (TRRL).

### 2.1.2 Catchment Location and Description

The length of motorway under study consisted of a 200 m straight stretch of the southbound carriageway of the M1 between junctions 11 and 12 in Bedfordshire. The location of the site with respect to Luton and surrounding areas is shown in Fig. 2.1. The site itself was about 56 km from Imperial College. The land use immediately surrounding the site was agricultural, but some heavy industry (car manufacturing) was located approximately 3 km to the west. A general impression of the appearance of the site can be gained from Figures 2.2 and 2.7.

Figure 2.3 shows the principal features of the site itself and a typical cross-section. The length of motorway under study comprised three travelling lanes of total width 11.1 m and hard shoulder of width 3.7 m, giving a total catchment width of 14.8 m. All four lanes were identically surfaced with hot rolled asphalt. The cross-carriageway and longitudinal slopes had gradients of 2.5 and 0.61%

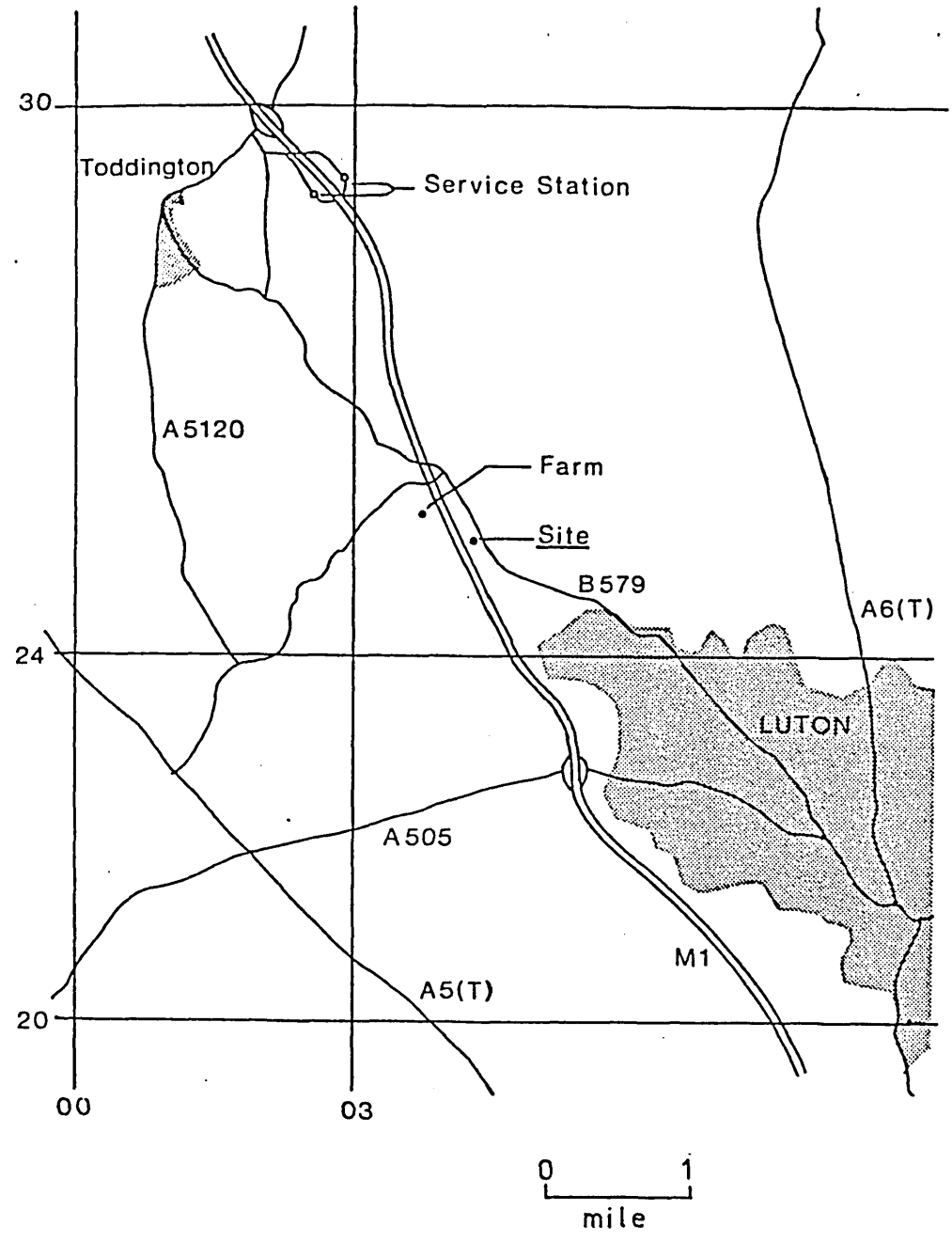



Figure 2.1 Location of sampling site showing ordnance data

Figure 2.2 (plate): General view of part of the carriageway catchment and verge, showing instrument hut A (centre). Camera is facing north.



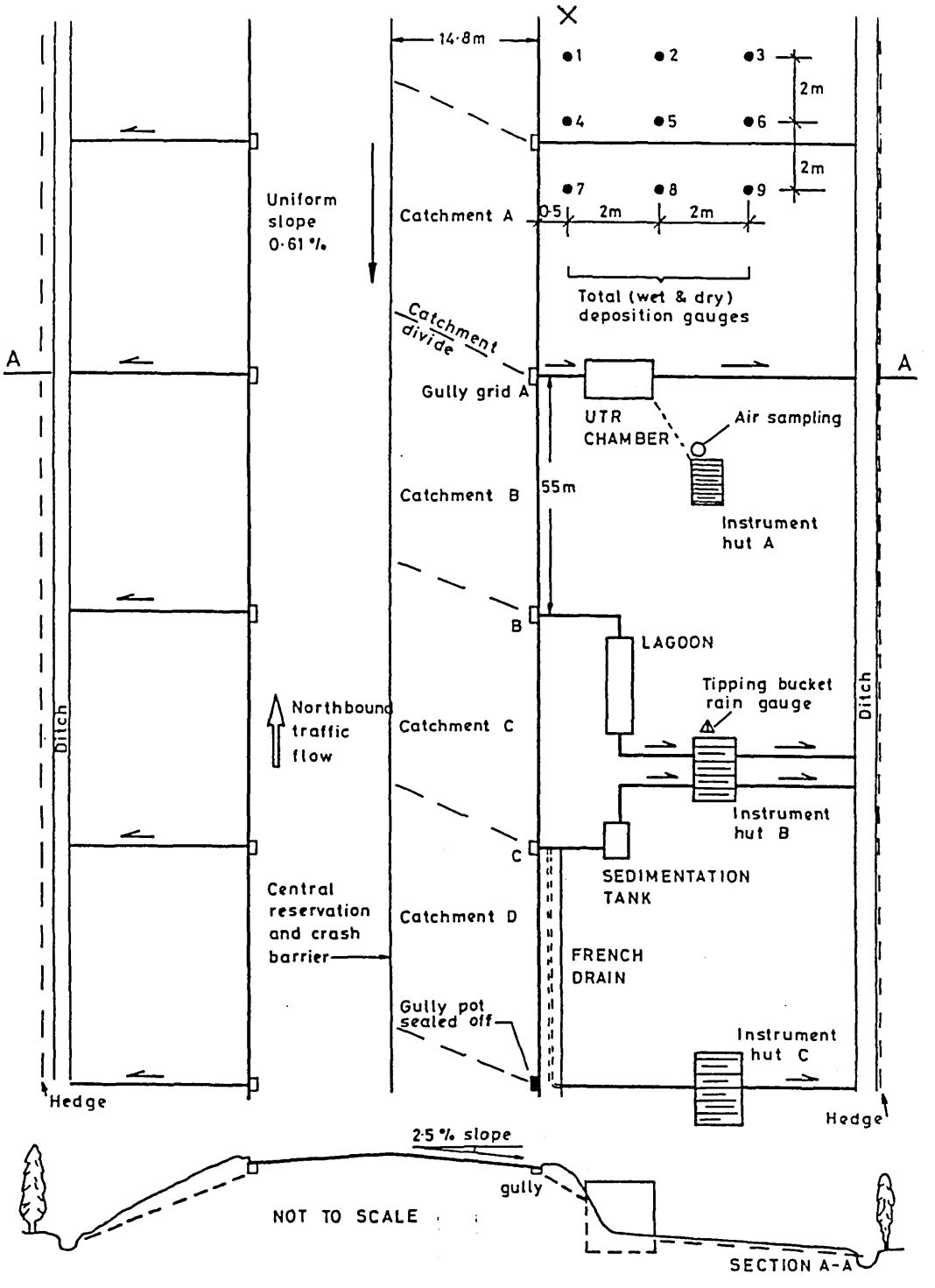



Figure 2.3 Plan and cross-section of the sampling site ('X' at top of diagram denotes beginning of embankment)

respectively. The edge of the tarred area was delineated at the edge of the hard shoulder by a continuous 100 mm deep 60° sloping kerb face, except for catchment D( Fig. 2.3) where it was removed to allow runoff to flow directly into the French drain. The central reservation bordering the opposite side of the carriageway had a porous surface and was separately drained, as was the northbound carriageway. The point 'X' in Fig. 2.3 marks the approximate beginning of an embankment carrying the entire length of carriageway under study, which became progressively higher in the southerly direction, and extended well beyond the end of the site.

The total area from which runoff was collected is a parallelogram with sides ~220 m along the edge of the carriageway and 15.2 m across, area ~3200 $m^2$. Gully pots were situated at approximately 55 m intervals along the kerb edge, thus dividing the area into four similar catchments of area ~800 $m^2$ (A-D, Fig. 2.3). Prior to modification for experimental work, all gully pots were connected by straight lengths of buried clay pipe (nominal ID 150 mm) to the drainage ditch on the eastern side of the motorway area. It will be noted in Fig. 2.3 that the embankment began at a point beyond the northern end of the catchment, thus preventing any runoff entering the study catchment from verges etc. The minimal longitudinal slope and general topography of the surrounding area gave the site area a generally uniform relief.

### 2.1.3 Summary of Site Attributes

In the light of the catchment criteria discussed in section 2.1.1, the essential features which made the M1 site suitable for the present work were uniform slope (owing to its linear nature), uniform surface cover, clearly defined catchment boundaries (owing to the raised position on an embankment), limited drainage area (794 $m^2$), uniform site relief and a rural surrounding area. Uniform slope and cover ensured minimum interference with water flow across the catchment to the kerb and thence to gully grids. Depression storage prior to the grids was at an absolute minimum. Clear definition of catchment boundaries, with separate drainage of all non-carriageway areas, virtually eliminated non-motorway sources of surface runoff on the catchment. The limited catchment area and uniform site relief mini-

mised spatial variation in precipitation and other environmental factors over the site area. This was especially important in work comparing treatment systems within the site area. The rural surroundings helped to minimise non-motorway contaminant inputs to the catchment. Practical advantages of the site position were that, owing to its super-elevated position, a workable head of water was created at all sampling points, simplifying flow measurement and sampling requirements. The associated steepness of the embankment sides and the position of the sampling facilities immediately adjacent to the edge of the catchment were expected to ensure minimal in-conduit deposition and turbulent flow, thus giving reasonable homogeneity of suspended solids content immediately prior to sampling.

The main penalities associated with use of this site were the distance from Imperial College (~56 km), and the small volumes of runoff generated during storms. The first penalty placed a practical limit on the frequency of site visits and therefore, on many occasions, runoff samples inevitably had to remain standing for several days at the site between sampling and collection. Low volumes of runoff meant that flow measurement and sampling techniques had to be modified accordingly. Sections 2.2-2.5 following describe detailed aspects of the techniques adopted in the light of these constraints.

## 2.2 Description of Drainage and Treatment Installations

### 2.2.1 Background

The site as used for the present work was built in the summer of 1980 by Bedfordshire County Council, to permit the study of the effectiveness of various methods of treating motorway runoff water. Design of the treatment installations themselves was undertaken by the Department of Transport (DTP), but selection of flow monitoring and sampling equipment was undertaken by the author, who was also responsible for ensuring that details of construction work were compatible with the proposed flow monitoring and sampling regime. Between 1976 and 1980, Pope and other workers carried out various studies on untreated runoff at the same location as the present site, and details of some of these studies have been published elsewhere (Graham, 1977; Pope et al., 1978a, Pope et al., 1978b; Pope et al., 1979). The present work was concerned chiefly with the quality of untreated runoff

from the site, and was an essential basis for simultaneous assessments of treated runoff quality undertaken mainly by other workers (Ofori, 1984a).

### 2.2.2 Untreated Runoff

Runoff from catchment A (Fig. 2.3) was treated as a control for the other catchments and was not subject to any treatment. All runoff from this catchment passed through gully grid A and was led directly *via* 150 mm ID PVC soil pipe, approximately 2 m in length, to a chamber containing flow measurement equipment, which is described in Section 2.3.2. (All plastic pipework used for carrying runoff at the site was standard commercially available "Osma" or "Terrain" PVC soil pipe, ID as specified in text or diagrams).

The original gully pot at this location (and at locations B and C) was modified to minimise depression storage between the gully grid and outlet pipe by infilling with mortar to the level of the outlet pipe invert. The dimensions of the grid were 0.35 m × 0.49 m, and the depth from the top surface of the grid to the level of the outlet invert was 0.45 m. A small tarmac berm was laid across the downstream side of the grid, joining up with the kerb, to prevent water flowing past the grid during high intensity events.

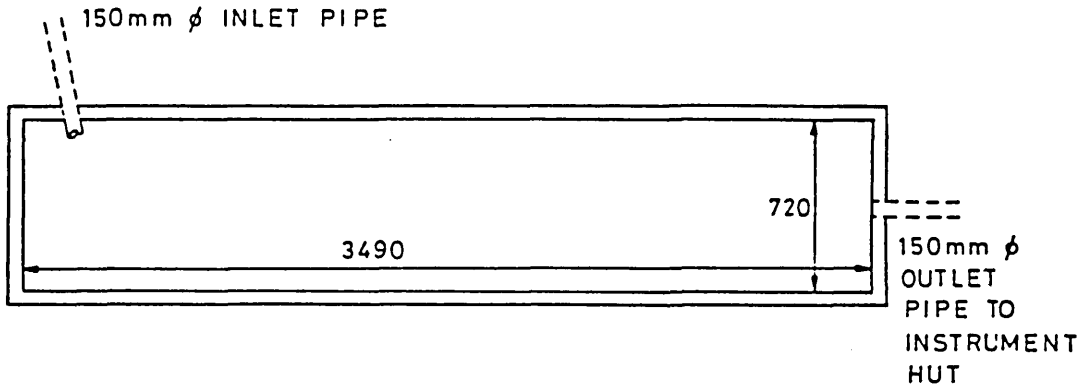
### 2.2.3 Sedimentation Tank

Runoff from catchment C was led *via* a 2 m length of 150 mm ID PVC pipe to a sedimentation tank (ST) made of internally rendered concrete blocks, with internal dimensions of 3.49 m (length), 0.72 m (width) and 0.9 m (depth), shown in Figs. 2.4 and 2.5. The inlet and outlet pipes were 0.60 m and 0.58 m respectively from the invert of the tank, giving a nominal holding capacity of 1450 l. The chamber was covered to prevent the entrance of direct precipitation and surface runoff from the verge. Flow from the outlet pipe passed directly to instrument hut B for sample collection and flow monitoring.

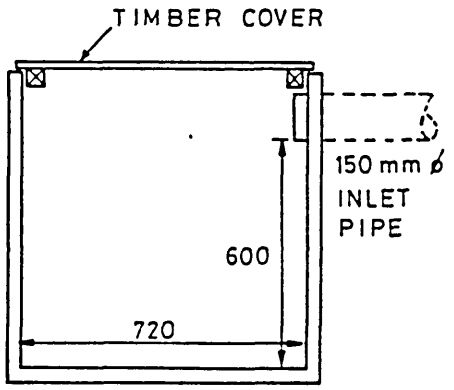
### 2.2.4 French Drain

Runoff from catchment D entered the french drain (FD), which consisted of a 50 m long vitrified clay pipe 150 mm in diameter with 6.25 mm diameter perforations 150 mm apart along two longitudinal rows. The pipe was 75 mm above the base of the drain and was covered

SEDIMENTATION CHAMBER




PLAN

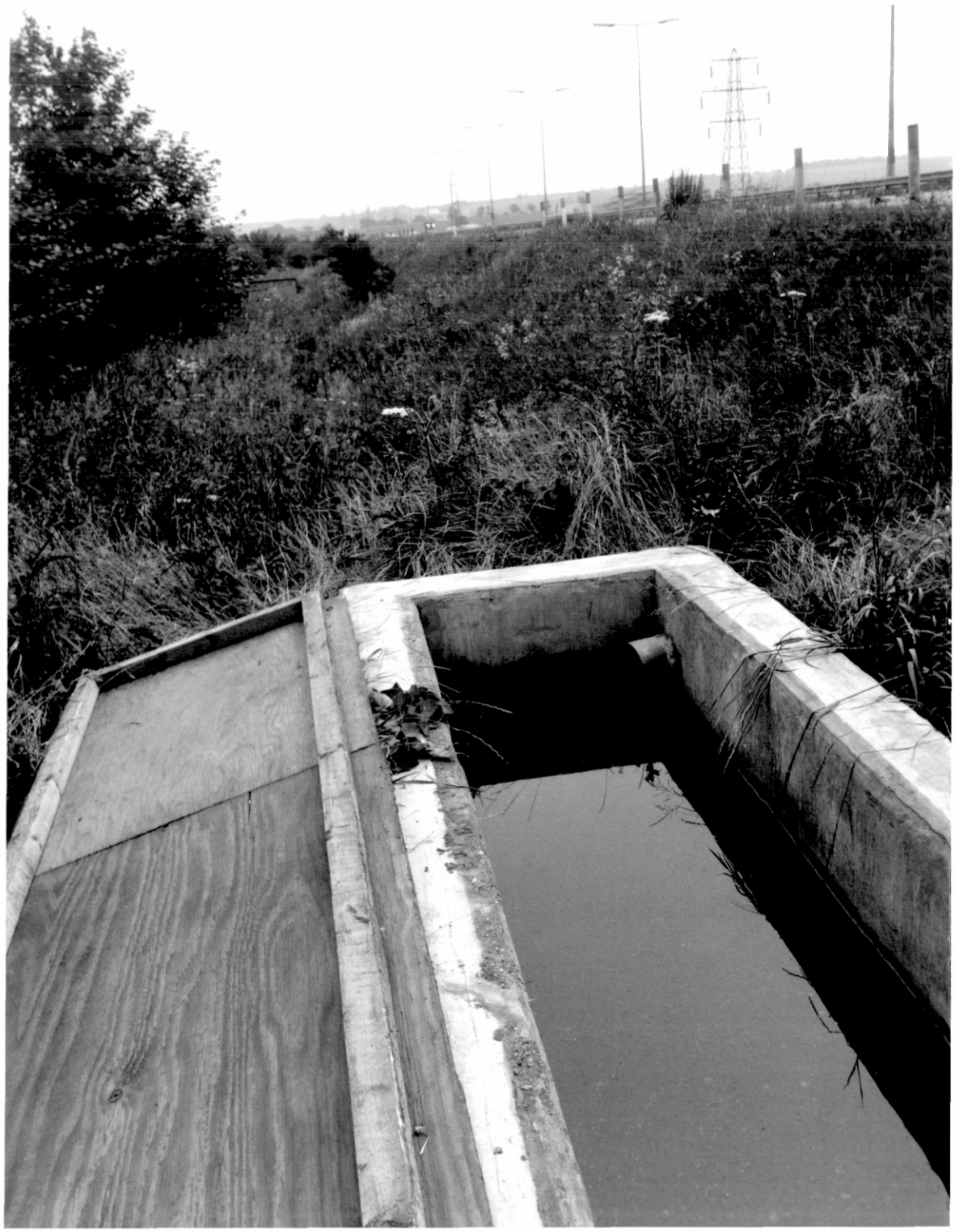



SECTION (Slighly enlarged)

All dimensions are in mm.
NOT TO SCALE

**Figure 2.4 Plan and cross-section of the sedimentation tank**

Figure 2.5 (plate): View of sedimentation tank showing inlet pipe.



to a depth of 1.2 m with Type B granular material of the specification presented in Table 2.1. The drain was lined with a 1.5 mm polyethylene sheet to prevent infiltration. A cross-section of the french drain is shown in Fig. 2.6 and a longitudinal view in Fig. 2.7.

TABLE 2.1 : Type B granular media specification (Department of the Environment, 1976)

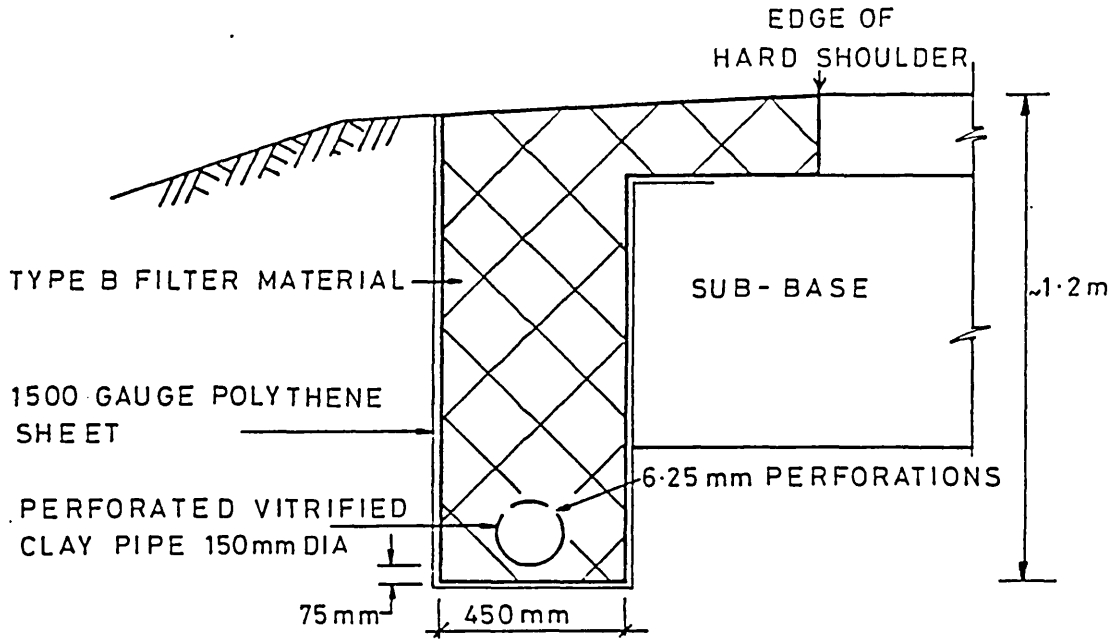
| BS Sieve Size mm | % by Mass Passing |
|---|---|
| 63 | 100 |
| 37.5 | 85-100 |
| 20.0 | 0-20 |
| 10.0 | 0-5 |
| 3.35 | - |

The existing gully pot was sealed off and the kerb along the edge of the hard shoulder removed so that surface water ran off directly from the road into the drain. The runoff percolated through the granular media, collected in the perforated pipe and then flowed into instrument hut C for flow measurement and sampling.

## 2.3 Flow Measurement

### 2.3.1 General

The characteristics of the catchment described in Section 2.1 meant that flow response to precipitation was rapid, but the actual volumes of flow to be dealt with were relatively small. An estimate of the upper limit of flow rates likely to be encountered from one 55 m long catchment at the site was made by Graham (1977) using the Bilham formula. From this it was considered that rates of up to 9 $ls^{-1}$ should be catered for. Narrow V-notch weirs used by Pope *et al.* (1978a) were found to be a satisfactory means of measuring the range of flows encountered, and the same type of unit was therefore chosen for the present work.




NOT TO SCALE

Figure 2.6 Cross-section of the french drain

Figure 2.7 (plate): Longitudinal view of french drain and part of associated catchment. (Note shallow berm at bottom right to prevent water run-over from adjacent catchment). Camera is facing south.



2.3.2 Design, Construction and Calibration of Weirs

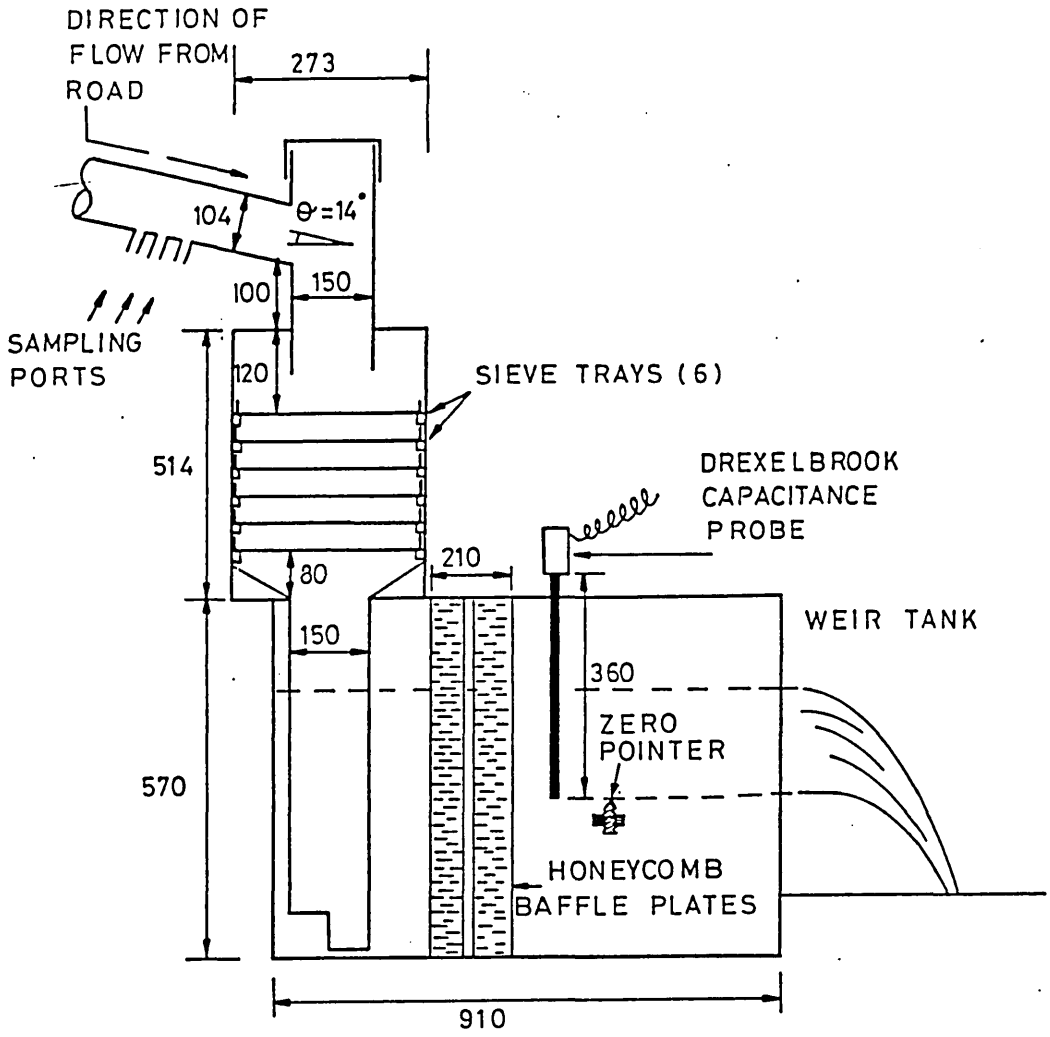
The same basic design of weir tank and V-notch was utilised for monitoring flow from catchments A, C and D. During design, extensive reference was made to British Standards Specification 3680 (part 4A), "Thin plate weirs and venturi flumes" (British Standards Institution, 1965). Space restrictions at the site meant that size criteria specified in this standard could not be followed rigorously, but since it was intended to calibrate weirs at Imperial College before installation on site, this was not considered to be a serious problem.

Pope et al. (1978a) had employed V-notch sizes of 60° and ½90° (53°), but when these were first installed he had no detailed knowledge of expected flow ranges, apart from Graham's estimates (1977). Thus it was necessary to make generous allowance in choosing V-notch size for the highest likely flows to be expected. In the event these sizes proved, if anything, to be larger than necessary - in 196 events reported by Pope (1979a), the highest flow recorded was 2.4 $ls^{-1}$. Following short preliminary trials with the first new weir tank constructed, the size of notch chosen for this work was (nominally) ¼90° (28°), 20.5 cms deep, giving a maximum measurable flow of 6.35 $ls^{-1}$.

The tanks themselves were modifications of standard galvanised steel water cisterns 0.91 m long, 0.61 m wide and 0.57 m deep. Figure 2.8 shows in diagrammatic form the construction of the weir tank and associated equipment used to monitor untreated runoff (UTR) flow, and Figs. 2.9 and 2.10 show the equipment as installed in a specially constructed chamber. The basic features of the equipment visible in Fig.s 2.8-2.10 are:

(i) A 100 mm ID pipe carrying flow from the outlet of the gully (not shown) to a vertical weir feed pipe which terminates ~50 mm above the base of the tank (Fig. 2.8). A sieve tray box incorporated into the vertical feed pipe is visible in Figs. 2.8-2.10. This is part of the runoff sampling equipment and is described separately in section 2.4.1(b).

(ii) Honeycomb baffle plates immediately in front of the feed pipe to assist dissipation of flow energy and reduce turbulence.




All dimensions in mm
NOT TO SCALE

Figure 2.8 Untreated runoff weir and sampling equipment

Figure 2.9 (plate): Interior of untreated runoff wier and chamber, showing inlet pipe, sieve trays and box, Drexelbrook probe and baffle plates.



Figure 2.10 (plate): View of untreated runoff weir, showing sieve tray box (left), top of Drexelbrook probe (centre) and V-notch weir plate.

(iii) A head measuring device, in this case a capacitance probe (Drexelbrook Engineering, Pennsylvania, USA).

(iv) An adjustable zero pointer used for accurate calibration of the weir (Fig. 2.8).

(v) A 28° V-notch weir plate fitted to the front of the tank (Fig. 2.10).

The ST and FD weirs were similarly constructed and installed in their respective site huts (Fig. 2.3), except that air reaction/dip tube systems of head measurement were used. The dip tube is clearly visible in the plate of the FD weir in Fig. 2.11.

The notch size selected was chosen primarily to suit flows of UTR. It was considered, however, that some flow attenuation would take place with the other two treatment systems so that the ranges of flow found there would not be in excess of those encountered with UTR. All three weirs were therefore fitted with similar 28° notches, which simplified construction and fitting.

Prior to installation of weirs on site, all weir tanks were calibrated to obtain an accurate rating curve (head-to-flow relationship) for the range 0-5 $ls^{-1}$ which could then be utilised for calibration of flow recorders.

Since $\log_{10}$ head is linearly related to $\log_{10}$ flow in a V-notch weir, the best fitting straight line to the data was obtained by least squares linear regression. Full details and a typical calibration curve are given in Appendix 1.

### 2.3.3 Flow Recording Equipment

#### (a) Untreated Runoff

The capacitance probe illustrated and referred to previously (section 2.3.2) was connected to a transmitter unit located in Hut A (Fig. 2.3) by buried coaxial cables. The principle of operation was that the probe acted as a device for measuring the electrical capacitance of the probe-water-tank "system". The transmitter unit output was adjusted using the flow rating curve previously derived (section 2.3.2) so that 4 mA corresponded to zero head (and flow) and 20 mA to

the probe immersion corresponding to maximum flow (5 $ls^{-1}$). Changes in mA output were recorded continuously on a strip chart recorder, and since the probe and transmitter unit were constructed so that changes in mA output were linearly related to flow when used with a V-notch weir, flows could be deduced directly from the chart.

(b) Treated Runoff

Flow monitoring and sampling of treated runoff from catchments C and D was carried out using units containing integated flow recording, sampling and sample bottling equipment (Bestel-Dean Ltd., Manchester, UK). The flow recorders (Type AR100F) operate on the air reaction/dip tube system. Figure 2.11 shows the dip tube in position on the FD weir, while Fig. 2.12 shows the front of two of the flow recording and sampling units, with the recorders clearly visible at the top of the units. A small pump inside the recorder provided a steady stream of air to the dip tube. Changes in pressure with head of water in the tank were detected and converted electronically to produce a linear head-to-flow response, which was recorded continuously on a strip chart to produce a hydrograph of each event. Weir calibration data were sent to the manufacturer prior to equipment delivery so that the recorders could be calibrated appropriately. On delivery, only a small zero adjustment was necessary once the recorder was connected to a dip-tube assembly.

## 2.3.4Installation of Flow Measuring Equipment on Site

### (a) Untreated Runoff Weir and Equipment

As shown in Figures 2.9 and 2.10, the weir and probe were accommodated on site in a block-built chamber, and a general impression of its size can be obtained from the figures. The rear chamber wall was 2 m horizontally from the gully grid. Once placed in the chamber in the position shown, the tank was carefully levelled and its position then fixed with mortar. When this had set, the tank feed pipe was connected to the chamber inlet pipe *via* the sieve tray box to produce the arrangement shown. The zero pointer of the weir was checked, and the probe installed as illustrated (Fig. 2.9) with the tip just touching the water surface at zero head. Probe cables were led to the adjacent instrument hut A *via* buried PVC pipes.

Figure 2.11 (plate): Close-up of french drain weir tank, showing, from left to right, feed pipe with slide-in circular sieve mesh holder for sampling bulk suspended solids, baffle plates to reduce turbulence in weir, and dip tube.



Figure 2.12 (plate): Front view of Bestel-Dean flow recorders (top), sampling unit (middle) and bottling units (bottom).



(b) Treated Runoff Weirs and Equipment

The installation of weir tanks in huts B and C followed a procedure similar to that described for the UTR weir. Dip tube air supply lines were led from flow recorders to dip tubes in a continuous falling gradient to avoid formation of condensation traps.

## 2.4 Runoff Sampling

### 2.4.1 Untreated Runoff

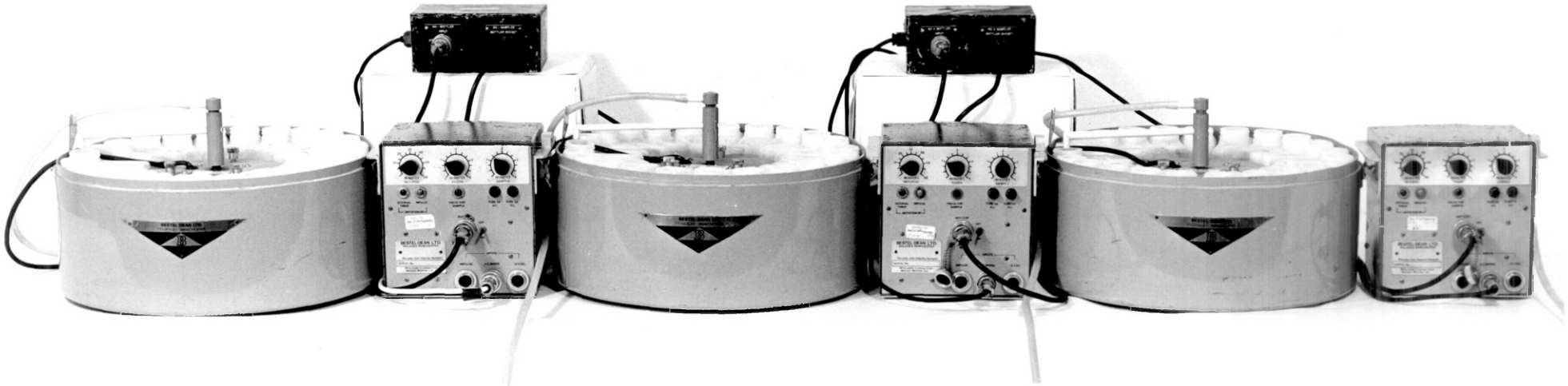
(a) Water Samples

Sampling of UTR was carried out via three stainless steel sampling ports tapped into the base of the 100 mm ID pipe carrying flow to the weir tank. This arrangement is shown schematically in Fig. 2.8. Each port was connected to a separate Bestel-Dean Mk III peristaltic pump and bottler in hut A by a length of buried 6 mm ID silicone rubber tubing. Each bottler held 24×500 ml sample bottles. The complete sampling system is shown clearly in Fig. 2.13 as set up in the laboratory. Sampling was initiated by an alarm circuit within the flow recorder (Section 2.3.3(a)) operated by the mA output from the Drexelbrook transmitter unit. When flow reached a pre-set value (usually about 0.1 $ls^{-1}$) the increase in transmitter output triggered the alarm circuit and mains power was supplied to the first sampler. Samples were then taken at time intervals pre-set by adjustment of controls on the front of the pumps. The three samplers and bottlers were electrically interconnected so that when the first bottler was full (i.e. 24 samples taken) power was then fed to the second sampler and then to the third. The recorder alarm circuit was usually set so that power to the samplers was cut off once flow fell below about 0.03 $ls^{-1}$. Sampling lines were cleaned by back flushing between each sample cycle. Flow velocity in the sample tube was 0.3 $ms^{-1}$.

(b) Bulk Suspended Solids

Facilities for obtaining bulk suspended solids samples from UTR can be seen on top of the weir in Fig. 2.9. This facility permitted the collection of larger amounts of suspended solids for additional experiments than could be obtained from 500 ml water samples, and also permitted rapid comparison of the solids content of treated and

Figure 2.13 (plate): View of Bestel-Dean Mark III samplers, showing bottling units, peristaltic pumps and electrical connecting boxes.



untreated runoff when used in conjunction with similar facilities installed at huts B and C.

The apparatus consisted of a large perspex box (Figs. 2.8 and 2.9) fitted between the top of the weir tank and the end of the inlet pipe. The box contained six square stainless steel trays (270 mm × 270 mm × 35 mm deep), the base of each tray consisting of a light framework supporting a square of stainless steel mesh. The area of mesh not excluded by framework was 676 $cm^2$. The trays were arranged in the box to give a downward sequence of mesh sizes of 1600, 400, 318, 253, 154 and 100 μm. Flow from the inlet pipe was directed into the centre of the top tray and after passing through the trays fell directly into the weir tank. Access to the sieves was by means of a watertight door in one side of the box. Provision was made for overflow in the event of a tray becoming blocked. Up to about 250 g of suspended material could be collected in this way without any blockage.

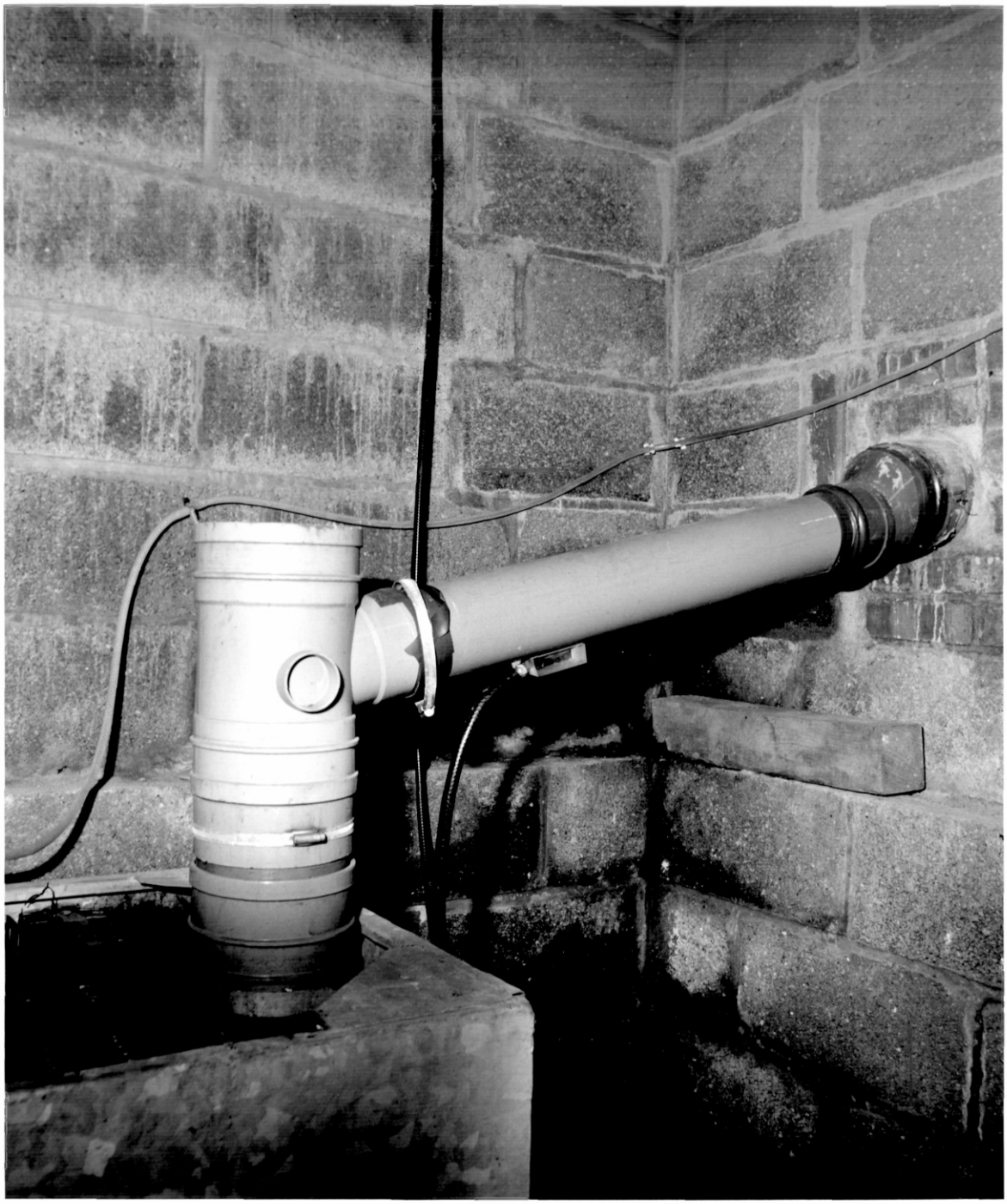
### 2.4.2 Treated Runoff

#### (a) Water Samples

The sampling systems used for ST and FD effluent were an integral part of the Bestel-Dean systems previously referred to in Section 2.3.3(b). In each unit, the sampler itself was mounted on the equipment frame directly beneath the flow recorder, and can be seen in Fig. 2.12. Samples were taken from the weir inlet pipe *via* a stainless steel tube of ID 9.5 mm tapped into the "downstream" end of a rectangular perspex block glued over a slot in the invert of the inlet pipe. This arrangement can be seen in Fig. 2.14 as fitted to the ST. A slot cut into the perspex block allowed runoff flowing down the pipe to pass to the sampling point, which was angled at 30°C to the line of the pipe to minimise air intake during the sampling cycle. A reinforced PVC pipe led from the sampling port to the sampler. Flow velocity in the sampling tube was 1 $ms^{-1}$.

The samples employed at each drain were Bestel-Dean VS100 models utilising a microprocessor-controlled vacuum sampling facility, partially visible in Fig. 2.12 (centre). Sampling in the standard VS100 model was initiated by a flow proportional input pulse from an accompanying AR100 flow recorder, but for the present work this was

Figure 2.14 (plate): Close-up view of sedimentation tank weir inlet, showing position and angle of sampling point (centre, attached to invert of inlet pipe).



modified to initiate time-related sampling once flow had reached an initial pre-set value, usually 0.05-0.2 $ls^{-1}$. Samples were then taken every 5, 10 and 20 mins. Samples collected in the sample chamber by vacuum were deposited in 500 ml bottles (24 in total) carried on a circular turntable below the sampler (Fig. 2.12).

(b) Bulk Suspended Solids

As with UTR, the weir inlet systems for treated runoff were also modified to permit sampling of the bulk flow for suspended solids, but on a more limited basis than with UTR due to space limitations. Sampling was carried out using a circular perspex frame designed to hold two flat circular pieces of stainless steel mesh 20 mm vertically apart in the line of the weir feed pipe. Figure 2.15 shows details of the sieve holder and Fig. 2.16 shows the holder as fitted into a weir tank inlet. The holder can also be seen in position in Fig. 2.11. The clear mesh area was 133 $cm^2$.

## 2.5 Additional Monitoring and Sampling

### 2.5.1 General

The equipment described so far in this section has been entirely concerned with runoff flow monitoring and sampling. In view of other objectives of the project (Section 1.4), it was necessary to undertake monitoring and sampling of additional parameters, and the need to elucidate background sources and levels of Br, Pb and other parameters at the site necessitated sampling of total (wet and dry) deposition, ambient air and, on a more limited basis, road surface dust, tyre rubber samples, road surface material from the site area and samples of de-icing salt.

### 2.5.2 Total Deposition

A grid of nine simple totalising rain gauges was employed, positioned about 50 m north of hut A on a flat section of the verge (Fig. 2.17). The gauges consisted of polypropylene funnels (cross section 670 $cm^2$) fixed into polypropylene bottles. The gauges were arranged in a 3×3 grid, the first row being 0.5 m from the kerb, the second 2.5 m and the third 4.5 m. Distance apart of the rows parallel to the kerb was 2 m.

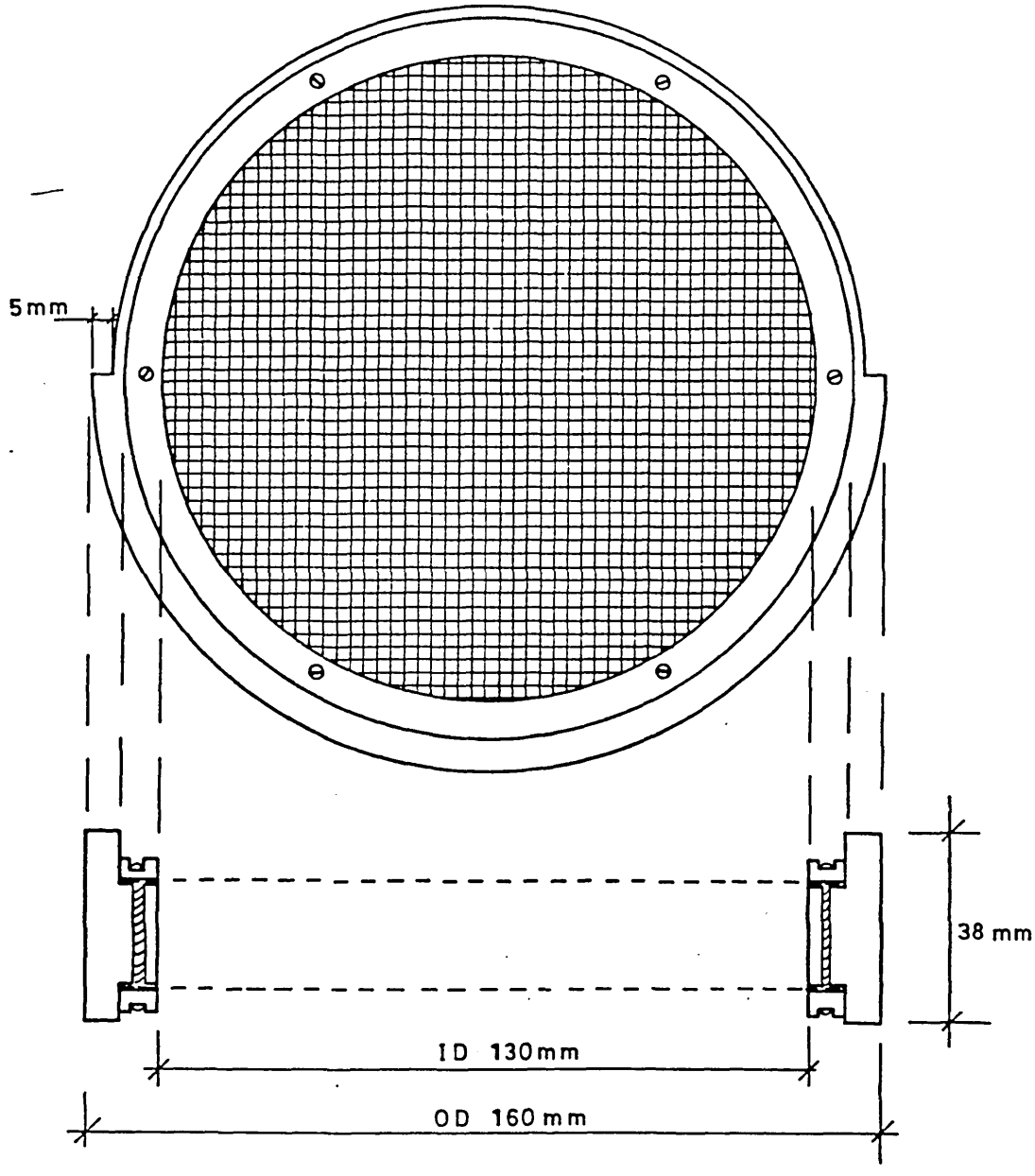



Figure 2.15 Sieve holder for treated runoff solids sampling

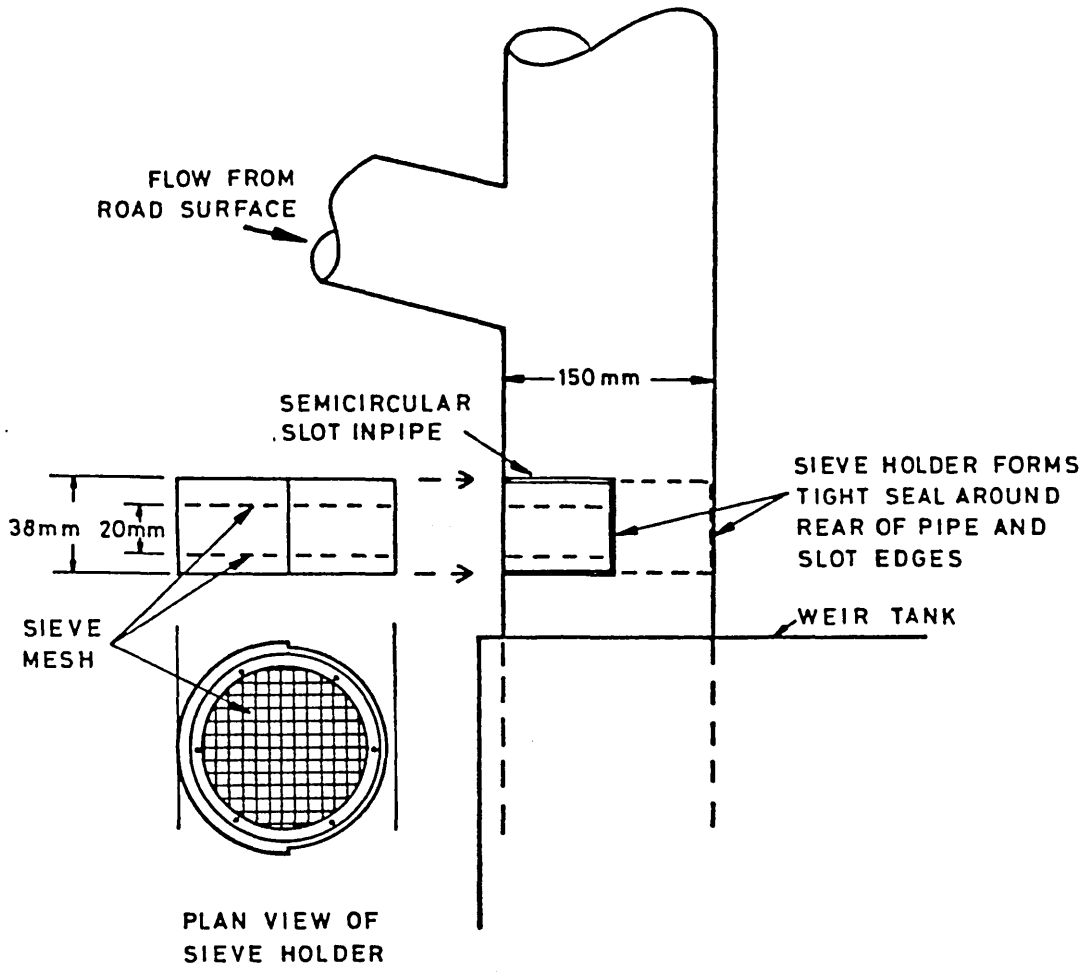



Figure 2.16 Sieve holder in position in weir feed pipe



Figure 2.17 (plate): Deposition sampling gauges
(Aluminium gauges at rear not used in this work).

Since no deposition gauge at the site could be placed further away than 11 m from the carriageway because of the boundary hedge, it was considered desirable to install a gauge in the site area but relatively remote from the motorway in order to gain a reasonably clear idea of background values for some of the parameters monitored at the site itself. A gauge was therefore established some 600 m west of the site at a nearby farm, consisting of a polypropylene funnel and bottle identical to those used at the site. Samples from this gauge were collected on the same day as samples from the site itself.

The equipment described above was not installed at the same time as runoff sampling equipment but several months later in May 1981. Samples analysed for this work were collected between May and August 1981.

### 2.5.3 Air Particulates

A programme of air sampling was carried out at the site between February and September 1981 to ascertain the ambient air concentrations of Pb and Br. Initially, particulate sampling only was carried out, but a modification to the sampling system was made at a later date in an attempt to trap non-particulate forms of Br.

The essential features of the system initially employed are shown in Fig. 2.18. The filter holder (on the right of the diagram) was protected from direct contact with rain by an inverted plastic container fitting tightly around the tube leading to the pump. The filter used was 0.22 μm cellulose membrane (Millipore, UK, Ltd.), 47 mm diameter, and the average pumping rate was 3 l $min^{-1}$. Silica gel, for minimising moisture entering the gas meter, was changed at the beginning of every sampling run. At the end of each sampling run, the used filter was transferred to a clean polystyrene beaker for return to the laboratory, and a fresh filter installed.

Once this system had operated satisfactorily for several months, a modification was made in an attempt to trap non-particulate Br species either present in ambient air or arising from decomposition of Br-containing Pb compounds already trapped on the filters. Following preliminary trials in the laboratory and at the site, a trap containing 500 ml of approx. 0.01 M (pH 12) KOH solution was installed

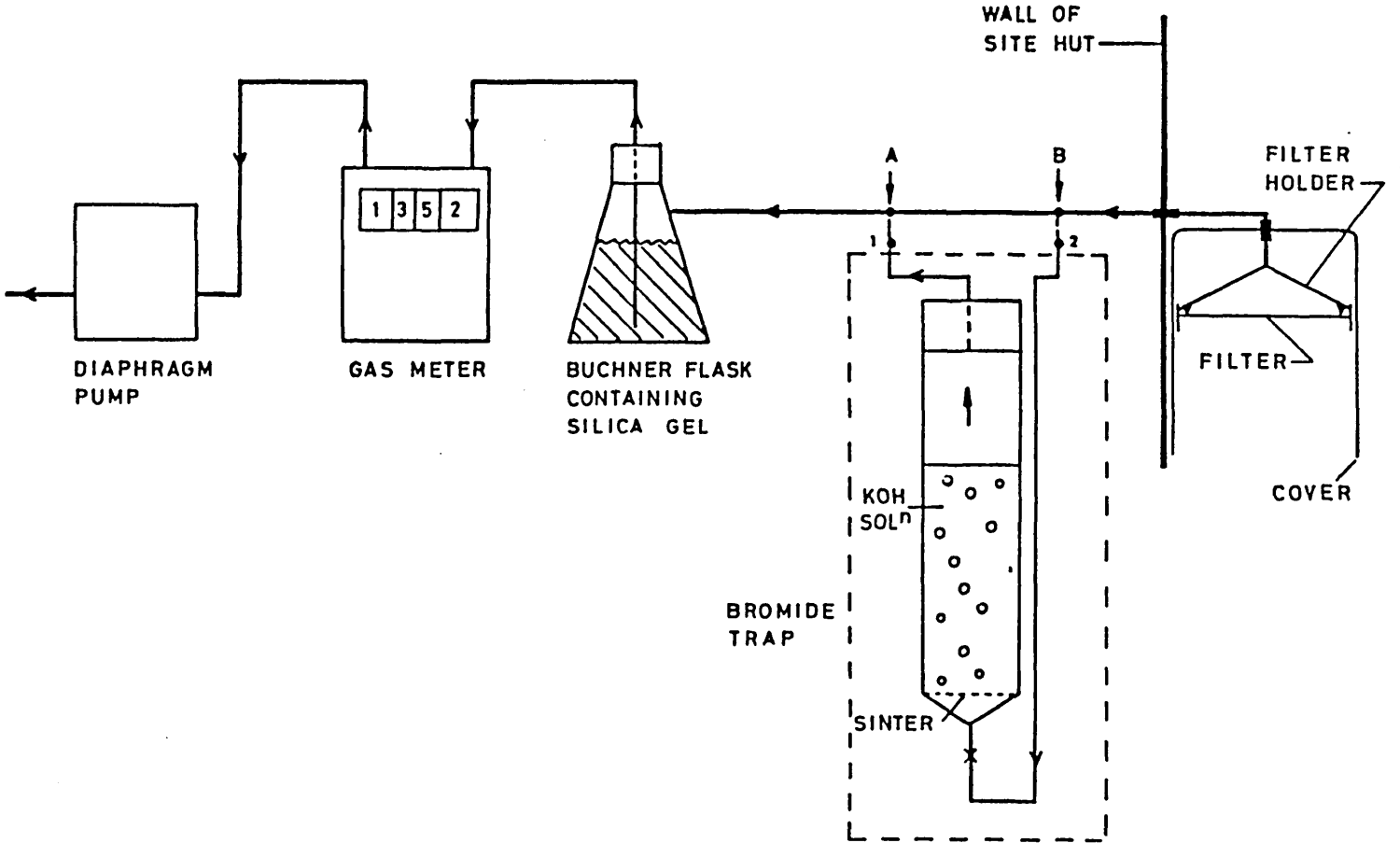



Figure 2.18 Air sampling apparatus

in the sampling system between the filter itself and the silica gel drying flask. An alkaline trap was used since it was considered that the most likely non-particulate forms of Br, if present, would be acidic in nature, e.g. HBr. Figure 2.18 shows the bromide trap (in outlined rectangle). By removing the air line between points A and B and connecting to points 1 and 2 respectively, the air flow from the particulate filter outside the hut was drawn through the base of a large glass sinter vessel containing the KOH solution as shown. Sampled air then passed through the remainder of the system, which was identical to that used for particulate-only sampling, except that a more powerful pump was employed.

The KOH solution was not replenished during a sampling run, but instead sufficient volume was added at the beginning of a run to leave between 100-200 ml in the vessel at the end. The volumes used for any particular length of run were found by trial and error during the first runs with this equipment. The approximate loss rate (due to evaporation) was 30 ml $day^{-1}$. At the end of a run, the remaining KOH solution was carefully decanted into clean, dry polystyrene beakers for return to the laboratory for later analysis. The sinter vessel was then rinsed well with deionised water, returned to an upright position with the tap closed, and 500 ml (approximately) deionised water poured in. Two or three pellets of 'Analar' grade KOH were then added, and the sealing cap replaced. The pump was then switched on and the tap opened sufficiently to provide a reasonable flow of air through the solution, usually between 2 and 6 l $min^{-1}$.

### 2.5.4 Other Types of Sample

Surface dust was collected simply by brushing dust directly from the surface into a polystyrene beaker placed sideways on the road, using a stiff, clean brush. Between 50 and 100 g could be collected in this way. The beaker was then capped prior to return to the laboratory. Road surface material was sampled by knocking small lumps off the edge of the tarmac bordering the french drain. Samples were wrapped in foil for return to the laboratory. Tyre rubber was sampled simply by collecting bits of tread lying on the verge and hard shoulder which had been lost by passing vehicles. Four bulk samples of de-icing salt were collected on a single occasion from the covered salt storage area at Toddington Motorway Maintenance Depot.

2.5.5 Traffic, Rainfall, Salting and Road Sweeping Data

Traffic data was supplied by TRRL from the two measuring loops nearest the site, one at Newport Pagnell, 23.2 km north, and the other at Friars Wash, 11.3 km south. The data consisted of hourly, daily and weekly totals of the total number of vehicles. There are several junctions between the two loops where the traffic may leave or join the motorway, however, and the Newport Pagnell traffic counts are almost always lower than those at Friars Wash, the average ratio between the two being about 0.8. No data was available on the relative proportions of traffic leaving or joining the M1 at these intermediate junctions, however, so traffic flow at the site was estimated by taking the arithmetic mean of the two figures. Where data from one of the loops was missing for any reason, an estimate was calculated from the mean ratio of Friars Wash and Newport Pagnell data for the same hour and day of the week for two weeks either side of the missing figure.

Monthly summaries of daily rainfall totals recorded at a Meteorological Office raingauge at Dunstable Cement Works, 3.22 km south west of the site, were provided by TRRL, Crowthorne, Berks. Additional quantitative data on local rainfall were available in the form of daily totals recorded with a tipping bucket gauge located 5.5 km north of the site at the Bedforshire County Council Motorway Maintenance Depot at Toddington Service Area. This occasionally provided useful information for identifying localised storms producing runoff which were not recorded at the Dunstable guage. Salting data were derived from records maintained at the Depot for each of two salting vehicles. Road sweeping information was also obtained from Depot records.

## SECTION 3. ANALYTICAL TECHNIQUES

### 3.1 Introduction

The main analyses carried out during the project can be summarised according to each sample type as follows:

Runoff : pH, electrical conductivity (EC), chemical oxygen demand (COD), Total solids (TS), total volatile solids (TVS), total suspended solids (TSS), $Cl^-$, $Br^-$, Pb, Zn and Cd

Deposition: pH, EC, TSS, $Cl^-$, $Br^-$ and Pb

Air filters: Br, Cl and Pb

Road dust, bitumen, tyre rubber: Br, Cl, Pb, Zn and Cd

Deicing salt: Insoluble solids content, $Br^-$, $Cl^-$, Pb, Zn and Cd

Sieve solids: Dry weight of solids, cyclohexane extractable organic ('oil') content, PAH, Pb

Bromide/bromine analyses (except in de-icing salt) were carried out using instrumental neutron activation analysis (INAA) techniques described in Section 3.9. Chloride/chlorine analyses in summer runoff, deposition, air filters, road dust, tyre rubber and bitumen were also carried out simultaneously with Br using the same INAA techniques. All other analyses are described in sections 3.2-3.8.

### 3.2 Runoff

#### 3.2.1 pH and Conductivity

The measurement of pH was performed using a combination electrode (CE7L, Russel pH Ltd., UK) in conjunction with a Digital Water Analyser (PTI 20, Data Scientific Ltd., UK) employing automatic temperature compensation. Prior to sample measurement, the electrode was calibrated using buffer solutions at pH 4 and 7. Every second or third sample was measured.

Conductivity was measured using a conductivity cell (K=1, Data Scientific Ltd., UK) in conjunction with the same Digital Water Analyser used for pH measurements. A thermocouple bead in the cell permitted automatic temperature compensation. Before sample measurement, the instrument was calibrated using 0.01 M KCl solution in distilled, deionised water.

### 3.2.2 Chemical Oxygen Demand

A standard method was employed, utilising oxidation with potassium dichromate and subsequent titration with ferrous ammonium sulphate (Department of the Environment, UK, 1972). Mercuric sulphate was used as recommended to suppress $Cl^-$ interference where necessary.

### 3.2.3 Total Solids and Total Volatile Solids

Total solids determination followed a standard method (Department of the Environment, UK, 1972) with some minor time-saving modifications. Following recommendations from previous workers (Pope, 1979b) the following modifications were adopted: after evaporation, 30 min oven drying of crucible plus contents and 30 min desiccator cooling followed by a single weighing. Sample volume was between 30 and 50 ml, taken immediately after vigorous shaking of the bulk sample.

Total volatile solids determinations followed on directly from the TS determinations, according to the standard method (Department of the Environment, op. cit.) ) without modifications.

### 3.2.4 Total Suspended Solids

Total suspended solids concentrations were determined by filtering a suitable volume of sample (usually 200-500 ml) through a 0.5 µm cellulose membrane filter (Oxoid Ltd., UK), followed by oven drying at 105°C for 30 min, desiccator cooling (30 min) and weighing. The filter assembly used was a three-piece filter funnel unit (Whatman Ltd., UK), consisting of an 80 mm ID borosilicate glass reservoir and funnel with a 90 mm diameter perforated polypropylene support plate. Between use, all parts were soaked in a 5% Decon 90 solution (Decon Laboratories Ltd., UK) overnight, then rinsed thoroughly, first wtih tap water, then with distilled water.

### 3.2.5 Chloride

Instrumental neutron activation analysis was used for determining $Cl^-$ in summer samples, as described in Section 3.9.1. This method could not be used for most winter samples, because of the

generally high sodium content leading to excessive $^{24}Na$ activity after irradiation. In these samples, therefore, $Cl^-$ was determined according to a standard method (Department of the Environment, UK, 1972) utilising titration of mercuric nitrate against a known volume of sample. Hydroquinone solution (1.0 g in 100 ml) was added (5 ml) to both sample and standard solutions as recommended during all titrations to suppress possible interference from ferric ions. Analyses were carried out on filtrates remaining after total suspended solids determination.

### 3.2.6 Lead, Zinc and Cadmium

#### (a) Instrumentation

Metals were determined by flame or flameless atomic absorption spectrophotometry (AAS). Flame determinations were carried using a Perkin Elmer Model 5000 atomic absorption spectrophotometer (Perkin-Elmer Ltd., UK) fitted with a 10 cm burner head, using an air/acetylene flame. Concentrations were automatically calculated from calibration data and recorded in digital form by a small printer attached to the instrument. The instrument was located in the laboratory of the Applied Geochemistry Research Group (AGRG) at Imperial College and analyses were carried out by AGRG technical staff. Flameless determinations utilised a Perkin-Elmer Model 603 atomic absorption spectrophotometer fitted with a HGA-400 heated graphite atomiser. Absorption signals were measured on a Perkin-Elmer Model 56 chart recorder. Analyses were carried out by the author.

#### (b) Glassware

All glassware used was borosilicate. Between use, it was soaked in 5% Decon 90 (24 h), rinsed with tap water, then leached in 1% (v/v) Analar nitric acid (24 h) followed by a thorough rinse with distilled water and a final single rinse with distilled, deionised water.

#### (c) Sample Pretreatment

Analysis of the total Pb, Zn and Cd content of the samples was carried out by determining the amount of each metal in the filtrable (filtrate) and non-filtrable (suspended solids) phases arising from the TSS determinations previously described, then combining the two

figures to gives the total. Filtrates and suspended solids required different pretreatment prior to analysis.

Filtrate sample (9 ml) was transferred by pipette to a 10 ml volumetric flask, and made up to volume with 10% (v/v) Analar nitric acid. The acidified sample was then analysed directly. Correction for the 9:10 dilution arising from acidification was made when calculating final concentrations.

Metals associated with suspended solids were solubilised by digestion of the solids with nitric acid and hydrogen peroxide before analysis, using a procedure based on that proposed by Krishnamurty et al. (1976). The membrane filter and solid residue was carefully halved, one half then being weighed and transferred to a clean, 150 ml tall form beaker. The remainder was stored for later INAA analysis. Concentrated Analar nitric acid was added (15-25 ml, depending on solids content in the sample batch) and the beaker contents simmered gently for approximately 2 h until near-dryness. After cooling for 15-20 min, Analar hydrogen peroxide (100 volume, 4 ml) was added and the digestion continued for another hour. The solution was then cooled and carefully transferred to a 50 or 100 ml clean volumetric flask and made up to the mark using 1% v/v Analar nitric acid.

(d) Analytical Procedure

Furnace conditions used for Pb analysis of runoff filtrates with the flameless instrument were based on published recommendations (Sterritt and Lester, 1980) but those actually employed were as follows:

| | | |
|---|---|---|
| Drying | : | 130°C for 40 s (Ramp time 10 s) |
| Ashing | : | 450°C for 40 s (Ramp time 5 s) |
| Atomisation | : | 2300°C for 5 s (Ramp time 1 s) |

Standards were made up by serial dilution of a 1000 $mgl^{-1}$ stock solution (Pb as Analar grade nitrate in 1% (v/v) Aristar nitric acid) to the required concentration. Standards of less than 10 $mgl^{-1}$ were made up on the day required, a range of 0-30 $\mu gl^{-1}$ usually being used. Samples and standards were injected into the furnace using a Finnpipette 2 step adjustable pipette (Jencons Ltd., UK), usually in 50 µl aliquots. Duplicate or, where necessary, triplicate injections

were made. The Pb absorption line at 283.3 nm was used for all flameless analyses. An approximate correction for signal suppression due to high NaCl content in some winter filtrate samples was made by reference to a standard curve of percentage peak height reduction vs $Cl^-$ concentration (obtained by analysis of a set of 20 $\mu g l^{-1}$ Pb standards containing chloride concentrations of 500, 1000, 2000, 4000, 5000, 6000 and 7000 mg $l^{-1}$ respectively) in conjunction with the filtrate $Cl^-$ concentration.

Digestates were analysed for Pb, Zn and Cd and filtrates for Zn and Cd by flame analysis. Samples were aspirated into the air/acetylene flame in the conventional manner. Absorption lines at 217.0 nm, 213.9 nm and 228.8 nm were used for Pb, Zn and Cd determinations respectively.

Background correction was used for all analyses on both instruments.

## 3.3 Deposition

### 3.3.1 pH, Conductivity, Total Suspended Solids, Chloride and Lead

Conductivity, pH, TSS and Pb were determined for samples and blanks according to procedures described for runoff samples (3.2.1, 4 and 6). Chloride was determined by INAA on filtrates (section 3.9.1) and suspended solids (section 3.9.2(b)).

## 3.4 Air Filters

### 3.4.1 Lead

Since only one filter per sample run was available for both Pb and Br analysis, each filter had to be carefully halved beforehand. The weight of the entire filter was first found, to an accuracy of ±0.1 mg. Using clean tweezers, it was then carefully broken into two halves, and the half used for Pb analysis weighed. This was then digested (15 ml concentrated Analar nitric) and analysed using flameless AAS as described (section 3.2.6). The remaining filter half was stored for later INAA analysis. Bromide trap samples were only analysed for Br and Cl using INAA (Section 3.9.1).

## 3.5 Road Dust

### 3.5.1 Particle Size Analysis

Air dried sample (~50 g) was sieved for 30 min on a mechanical shaker (Model EFL2, Endecotts Ltd., UK) using six 10 cm diameter ASTM standard stainless steel sieves of mesh sizes 500, 250, 150, 125, 63 and 38 μm (Endecotts, Ltd., UK) fitted with a collecting pan. After sieving, the subsamples on each mesh size and in the pan were weighed.

### 3.5.2 Metal Content

From each subsample produced by the particle size analysis (section 3.5.1) a smaller sample (~400 mg) was produced by coning and quartering. From each of these, two subsamples (50 mg) were taken for digestion and metal analysis as described in section 3.2.6(c) and (d). The remaining 300 mg was used for Br and Cl analysis by INAA (section 3.9.2(d)).

## 3.6 Tyre Rubber and Bitumen Metal Content

These samples were analysed for Pb, Zn and Cd content. Tyre rubber samples were prepared by cutting small lumps off the large pieces originally collected (Section 2.5.4) using a sharp, clean dissecting knife. All previously exposed surfaces of the small pieces were then removed, and their size trimmed until each piece weighed 100 g (approx). The pieces were then washed with distilled, deionised water and dried in an oven at 60°C for 1 h. After drying and weighing, pieces were digested and analysed using flame AAS in a similar manner to runoff suspended solids (Section 3.2.6).

Road surface material samples consisted of large granite chips (~1 g) held together by bitumen. Only the bitumen binder was analysed. This was prepared by breaking up the bulk sample using a screwdriver blade. Small pieces of bitumen were then broken off using a clean knife blade, and pieces of 100 mg with no previously exposed surfaces separated. The separated pieces were then washed with deionised, distilled water, dried, digested and analysed in the same way as tyre samples.

## 3.7 De-icing Salt

### 3.7.1 Insoluble Solids

Samples (4×50 g approx) were weighed to ±0.01g and added to 500 ml conical flasks containing 200 ml distilled water each. The samples were then left to stand at room temperature (24 h) to allow complete solution of the soluble content. Solutions were then filtered and suspended solids content assessed in a similar manner to runoff samples (Section 3.2.4). Solids content was calculated as percentage of original sample weight.

### 3.7.2 Bromide, Chloride and Metals

Analyses for the $Br^-$, $Cl^-$, Pb , Zn and Cd content of four different salt samples was carried out by the Analytical Services Laboratory, Imperial College. Bromide determination was based on the Kolthoff method (Kolthoff and Yutzy, 1937). Chloride was determined by Mohr titration (Department of the Environment, UK, 1972) and Pb, Zn and Cd by flameless AAS on acidified filtrate and digested solids after dissolving and filtering sample aliquots. Values were reported as weight percentage (Br and Cl) or ppm (Pb, Zn and Cd) of undried sample (i.e. "as applied").

## 3.8 Sieve Solids

### 3.8.1 Dry Weight of Solids

For both untreated and treated runoff samples, sieves containing the collected solids were placed on a clean surface, covered with tissue and left to air dry for at least a week. When dry, solids were scraped off each sieve with a plastic spatula onto a pre-weighed sheet of aluminium foil. Foil and solids were then reweighed to give the weight of solids by difference.

### 3.8.2 Cyclohexane Extractable Organic ('Oil') Content

#### (a) General

The term 'oil' is normally defined by the analytical procedure adopted (Peters and Perry, 1983) and in this work corresponds to the total cyclohexane extractable material present in the sieve solid samples. This definition means that 'oil' values do not correspond

solely to lubricating vehicle engine oil or free oil as commonly defined, but in the case of motorway runoff sediment this will probably constitute the single most important source of hydrocarbons on the road surface.

Oil content was determined as the first stage of a combined oil and PAH analysis. Since some PAH are volatile and sublime at low temperatures heating of samples during analysis must be avoided. For this reason an oil extraction method using a flask shaker was employed, rather than the conventional Soxhlet method, which requires heating. Comparisons between the two methods were first carried out, however, to assess the efficiency of the flask shaker method compared with the Soxhlet extraction.

(b) Solvent and Glassware

Cyclohexane was used for all oil extractions. This was first purified by fractional distillation and passing the distillate down an activated alumina column before collection. All glassware used was first soaked in 5% Decon 90 solution (24 h) followed by thorough rinsing with tap water, then distilled water.

(c) Flask Shaker Method

An approximately 2 g quantity of sample for each mesh size was obtained by coning and quartering the bulk sample. The subsample was then accurately weighed and placed in a 50 ml round bottomed flask. Purified cyclohexane (20 ml) was then added to the flask, which was then shaken vigorously using a flask shaker (Gallenkamp Ltd., UK) for 5 min. On settling, the supernatant extract was decanted and centrifuged for 5 min. The extract was then carefully transferred through a small glasswool filter pad to a carefully dried and weighed 250 ml round bottom flask. The extraction was then repeated three times, and the subsequent extracts added to the first 20 ml. The total extract was then concentrated using a rotary evaporator (Büchi AG, Switzerland) at a temperature not greater than 28°C followed by desiccator drying (24 h). The amount of oil extracted was then quantified by weighing.

(d) Soxhlet Method

Between 10 and 20 g of sample (obtained by coning and quartering) were placed in an extraction thimble (Whatman Ltd., UK) which was then fitted into a Soxhlet extractor. The extractor was fitted to a pre-weighed 100 ml round bottomed flask to which purified cyclohexane (~70 mls) had been added. The flask was heated with an electric heating mantle and the extraction carried out for 5 h. The resultant solution was then concentrated and the extract dried and weighed as for the flask shaker method.

3.8.3 Particle Size Analysis

Oil content was first extracted from ~20 g sample using the Soxhlet method described above. The residue and thimble were then dried in an oven at 60°C for 1 h, after which the dry residue was sieved and weighed in an identical manner to the road dust samples previously described (section 3.5.1), using mesh sizes of 500, 250, 150, 125, 63 and 38 μm.

3.8.4 PAH Determination

Six PAH (Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a) pyrene, Benzo(ghi)perylene, Fluoranthene and Indeno (1,2,3-cd) pyrene) in oil extracts were determined using two-dimensional thin-layer chromatography (TLC).

(a) Preparation of Thin-Layer Plates

Alumina Oxide G (18.6 g, Type 60/E; Merck, W. Germany) and acetylated cellulose (8 g, Type MN300, 40% acetylated; Camlab Ltd, UK) were placed in a 250 ml beaker and made into a slurry by adding ethanol (40 ml) and methanol (2 ml) followed by stirring. Clean 20×20 cm glass plates were then coated with the slurry to a thickness of 0.25 mm using a purpose-built plate spreader. After air drying, the plates were then activated in an oven (105°C) for 1 h, then stored in a desiccator until use.

(b) Standard PAH Solutions and Chromatograms

Primary standard solutions of the six PAH were prepared by dissolving 10 mg of each pure compound in cyclohexane (10 ml). These solutions were then diluted in cyclohexane to provide a range of concentrations of 5, 10, 20, 40, 60, 80 and 100 ng per 10 µl for each compound. Aliquots of 10 µl of the lowest standard (5 ng per 10 µl) of each compound were then spotted onto a corner of a TLC plate using a syringe. This process was then repeated for each of the six remaining standard concentrations on a separate plate each, giving seven plates in all. These were then developed in two dimensions orthogonally, first in a bath of hexane, then in a bath of methanol-ether-water (4:4:1 v/v), followed by air drying and storage in darkness until use.

(c) Sample Analysis

The oil extract derived from the flask shaker method (described in section 3.8.2(c)) was redissolved in cyclohexane (2 ml). A suitable aliquot (5-10 µl) was spotted onto one corner of a TLC plate and developed in a similar manner to the standards. The sample PAH content was then quantified by visual comparison of the fluorescent intensities of sample and standards under ultra-violet light of wavelength 366 nm.

3.8.5 Lead

Following oil extraction and sieving of ~20 g samples as described in 3.8.3 previously, subsamples (50 mg) from the solids retained on each mesh were digested and analysed for Pb in a similar manner to runoff suspended solids, as described in section 3.2.6.

3.9 Instrumental Neutron Activation Analysis for Bromine and Chlorine

3.9.1 Aqueous Samples

(a) Irradiation Conditions

All sample irradiation and counting was carried out at the University of London Reactor Centre (ULRC), Ascot, Berks. The reactor layout is illustrated in Appendix 2. Reactor facilities were available on a daily basis. In order to analyse as many samples as possible for both Br and Cl during a day's irradiations, a short irradiation (5 min), decay (5 or 10 min) and counting (5 min) scheme was

adopted, using the easily activated and short-lived isotopes $^{80}Br$ and $^{38}Cl$ ($t_{\frac{1}{2}}$ 17.6 and 37.3 min respectively) for counting. This scheme necessitated the use of the in-core irradiation system (ICIS), which allows rapid transfer of irradiated samples from the reactor core to counting equipment. Samples were placed at the core centre and irradiated for 5 min under a thermal neutron flux of $2.4 \times 10^{12}$ n $cm^{-2}s^{-1}$ and a fast flux of $1.0 \times 10^{12}$ n $cm^{-2}s^{-1}$. The isotopes $^{80}Br$ and $^{38}Cl$ were determined by measuring the γ-ray energies at 617 keV ($^{80}Br$) and 1642 keV ($^{38}Cl$).

Some samples containing high levels of sodium chloride could not be irradiated in this way because of the high activity induced due to $^{24}Na$, which, with $t_{\frac{1}{2}}$ of 15 h, was still far too active after 5 or 10 min decay to permit $^{80}Br$ counting. Such samples were placed in a cadmium tube and irradiated for 8 h under an epithermal neutron flux of ~ $1.0 \times 10^{12}$ n $cm^{-2}s^{-1}$, followed by 65 h decay before counting the $^{82}Br$ isotope at 777 keV. The cadmium shield decreases the induced activity of many nuclides (such as sodium) by a factor of 30 or more whereas that of Br is reduced by a factor of 2 or less (Lyong, 1964). Chloride cannot be determined using this technique.

(b) Counting

Short irradiation samples were counted for 5 min and long irradiation samples for 30 min using a Ge(Li) detector (Model 7500, Canberra Inc., USA) and appropriate signal processing equipment. The equipment layout is illustrated in Fig. 3.1. Dead time was kept to a maximum of 20% by adjusting the distance between sample and detector and by using a 10 min decay time for more active samples batches. Final output was in the form of teletype printout, giving the number of counts per channel over each spectral region of interest. Peak areas were calculated manually.

(c) Sample Preparation

Two primary considerations governed the choice of aqueous sample preparation technique. Firstly, the final form of the sample had to be appropriate for using the ICIS system and, secondly, rapid transfer from the irradiation container to a non-irradiated container was considered desirable before counting, due to Cl and possibly Br

Figure 3.1 (plate) : Counting equipment for neutron activation analysis showing Ge (Li) detectors (left, enclosed), signal processing equipment and monitor screen (centre) and teletype printout (right).


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impurities in the polythene containers used (Minski, 1980). Following some preliminary experiments with a variety of techniques, the following procedure was adopted.

Sample (100 ml) was freeze dried in a 150 ml polyethylene beaker (Payne Ltd., UK) containing a 55 mm diam. cellulose filter paper (No. 541, Whatman Ltd., UK) covering the base. The filter provided a support matrix for the residue and a similar physical matrix to standards (see following section). The solid residue was compressed into a pellet together with the filter paper and small pieces of additional No. 541 filter used to remove traces of residue from the beaker walls. The pellet was then enclosed in a clean, leached 15 mm diam. polythene capsule (Size No. 2, Gallenkamp Ltd., UK), and irradiated under the conditions previously described. The pellet was then transferred to a non-irradiated capsule before counting. Sample preparation was identical for short or long irradiations. Types of sample treated in this way were runoff, deposition and bromide trap solutions.

(d) Standard Preparation

Standards for short irradiations were made up from stock solutions of potassium bromide (10,000 $\mu g^{-1}$ as bromide) and potassium chloride (10,000 $\mu gl^{-1}$ as chloride), made up from the respective Analar grade salt. A known amount of each solution was placed on a 55 mm diam. Whatman No. 541 filter paper (by syringe or micropipette) and evaporated to dryness in a desiccator. After pelleting, the standard was enclosed in a clean, leached polythene capsule (Size No. 2, Gallenkamp Ltd., UK) for irradiation. Standards for long irradiations contained only bromide, but were prepared in the same way.

3.9.2 Solid Samples

(a) General

Irradiation conditions and counting procedures for solid samples were exactly the same as for the short irradiation (ICIS) samples previously described (Sections 3.9.1(a) and (b)). Sample preparation procedures depended on sample type, as described below, but standards were made up as previously described (Section 3.9.1(d)).

(b) Suspended Solids

Following the halving of a filter paper and suspended solids prior to metal analysis as described (Section 3.2.6(c)), the remainder was carefully folded, pelleted and enclosed in a polythene capsule (Size No. 2, Gallenkamp Ltd., UK) prior to irradiation.

(c) Air Filters

These were treated similarly to suspended solids, except that because of the low bulk of the original filter, half of a 55 mm diam. Whatman No. 541 filter paper was pelleted at the same time to produce a physically stronger pellet.

(d) Road Dust

Following sieving, coning and quartering as previously described (section 3.5) sample (100 mg) was weighed out onto a clean piece of aluminium foil and then transferred to the centre of a 55 mm diam. Whatman No. 541 filter paper. This was folded around the sample using tweezers and the whole pelleted and encapsulated as before.

(e) Tyre Rubber and Bitumen

Clean pieces of these samples of approximately 50 mg (tyre rubber) or 100 mg (bitumen) were prepared as described in Section 3.6, placed in polythene capsules (Size No. 2, Gallenkamp Ltd., UK) and irradiated directly.

# SECTION 4. NEUTRON ACTIVATION ANALYSIS FOR BROMINE IN MOTORWAY SAMPLES

## 4.1 Introduction

The objectives of the present work required the use of an analytical technique for Br at low concentrations which could be applied to a wide range of samples and which did not suffer from interferences from constituents which are commonly present in road runoff and other samples. Thus although a number of classical "wet" chemical techniques exist for $Br^-$ analysis in relatively unpolluted natural waters, neutron activation analysis (NAA) was considered particularly suitable for the present work because of the frequently contaminated nature of the samples and the applicability of the technique to both aqueous and solid samples. In addition, in most instances Cl could be determined simultaneously with Br, an additional advantage when comparison of sample Br and Cl contents is required.

### 4.1.1 Neutron Activation Analysis of Aqueous Environmental Samples

Neutron activation analysis (NAA) of trace elements in natural and polluted waters has received considerable attention in the past decade or so. The principles and general application of NAA have been comprehensively covered in several standard texts on the subject (Kruger, 1971; Amiel, 1981). In brief, the radioactive species produced following neutron-induced reactions during irradiation in a thermal neutron flux are quantitatively determined by means of $\gamma$-ray detectors (NaI(Tl) or Ge(Li) semi-conductor types) and multichannel analysers. Accuracy, precision, and detection limits are affected by irradiation conditions, sample pretreatment and background activity of the sample.

Many applications of NAA to water analysis utilise some form of post-irradiation chemical separation, but in recent years interest has grown in purely instrumental or semi-instrumental methods for routine simultaneous analysis of a wide range of elements, including $Br^-$ and $Cl^-$ in natural waters and, more recently, various types of effluent.

Purely instrumental NAA (INAA) has been applied to groundwater samples for the determination of 16 elements by Clemente and Matsinu

(1974) who irradiated their samples (10 ml) in quartz vials for 14 h in a thermal neutron flux of $2.6 \times 10^{12}$ n $cm^{-1}s^{-1}$. Counting for $Br^-$ determination took place 5 days after irradiation (100 min); $Cl^-$ was not determined. A detection limit of 2 $\mu gl^{-1}$ was given for $Br^-$ at a mean concentration of 70 $\mu gl^{-1}$, with a relative standard deviation (RSD) of 11% for triplicate determinations at 37 $\mu gl^{-1}$.

Salbu et al. (1975) conducted a more comprehensive evaluation of a similar technique, analysing a total of 40 elements in natural waters. Samples (5 ml) were irradiated in polythene or quartz containers (for short (10 min) or long (3 days) irradiations respectively). Short irradiation conditions were: irradiation for 10 mins at flux $1.5 \times 10^{13}$n $cm^{-2}s^{-1}$, decay 3 min, counting 10 min; long irradiations:irradiation for 3 days, decay 3 or 17 days, counting 15 min (3 day) or 60 min (17 day). After irradiation, sample containers were opened and sample rinsed into a clean container with dilute nitric acid before counting. Bromide was determined after 3 day irradiation and 3 day decay, $Cl^-$ using the short irradiation scheme. Detection limits were 0.05 $\mu gl^{-1}$ for $Br^-$ and 0.7 $\mu gl^{-1}$ for $Cl^-$, with a $Br^-$ blank of 0.26 $\mu gl^{-1}$ for polythene containers. Relative standard deviations (RSD) for four river water samples were 6% for $Br^-$ at 5.4 $\mu gl^{-1}$ and 3% for $Cl^-$ at 880 $\mu gl^{-1}$. More recently, Prest (1982) used a direct irradiation method for 10 ml samples of river water for analysing $Br^-$ concentrations in the 0-100 $\mu gl^{-1}$ range. Potential interference from $^{38}Cl$ ($t_{\frac{1}{2}}$ = 37 min), $^{24}Na$ ($t_{\frac{1}{2}}$ = 15 h) and $^{56}Min$ ($t_{\frac{1}{2}}$ = 2.8h) in the samples was avoided by using a 90 min irradiation followed by 3-5 days decay, prior to counting of the $^{82}Br$ ($t_{\frac{1}{2}}$ = 36 h) isotope.

Although these techniques have produced satisfactory results, it should be noted that, for all the $Br^-$ determinations referred to, a long irradiation and decay time has to be used. This can be a disadvantage if a high rate of sample analysis has to be carried out using limited access to irradiation and counting facilities, as with this work. Harrison (S.H.) et al. (1975) noted that another possible disadvantage of direct irradiation was insensitivity to elements at very low concentrations, while irradiating very large sample volumes is hampered by problems of flux variations, large sample blanks, and difficulties in calibrating the counting geometry. In an attempt to

overcome these problems, Luten et al. (1977) used an isotopic exchange technique in the analysis of rainwater for $Br^-$ and $I^-$. Irradiated samples were mixed with a solution of Br (as bromine) in $CCl_4$, and following exchange the activity in the organic phase was then counted. The detection limit for $Br^-$ was 1.0 $\mu g l^{-1}$, and the error for five replicate surface water determinations was ±10% at 300 $\mu g l^{-1}$. Chloride could not be determined in this way.

Harrison (S.H.) et al. (1975) carried out an investigation of freeze drying techniques for sample preconcentration, mainly on filtered samples containing radioactive tracers. Samples were contained in linear polythene bags during drying. The residue was resolubilised and compared with untreated sample. At least 95% of all elements except Hg and I were retained in the residue. Bromide was found to have an average retention of 99.3±1.7% in neutral solutions, but losses were reported (no data given) from solutions at pH 1.5 where Br was originally present as bromide. Chloride retention data was not reported, but this is presumably satisfactory. The study was extended by freeze drying river water samples, direct heat sealing of the bags and folding to a small volume (1 $cm^3$) for irradiation. This procedure eliminated losses involved in transferring freeze dried residues to irradiation containers, but a polythene film with a very low trace element concentration was essential for elements at very low concentrations. No data for $Br^-$ or $Cl^-$ were given on the river samples, however.

Lieser and Neitzert (1976) also studied freeze drying techniques on 200 ml water samples for determination of $Br^-$ and 20 other elements. Residue was irradiated for 1 day followed by 1 day decay. The detection limit for $Br^-$ was 0.02 $\mu g l^{-1}$. Reproduceabilities for $Br^-$ and other elements were only presented in the form of a graphical summary, but appeared to be satisfactory, and in general analysis by this means for $Br^-$ and several other elements was stated as being "without problems". Habib and Minski (1981) studied Thames river water using 1 l freeze dried samples which were irradiated for 35 h at a flux of $2.4 \times 10^{12}$ n $cm^{-2}s^{-1}$, with decay and counting times of 1 week and 50 mins respectively. The RSD of $Br^-$ concentrations for four replicates was 16.8% at an average concentration of 82.1 $\mu g l^{-1}$. Freeze dried residue was transferred to a capsule before irradiation. Luong et al.

(1983) applied a similar technique to 100 ml samples of natural waters and some sewage effluents. Freeze dried residue was pelleted with cellulose filter paper and encapsulated before irradiation. A precision of 2-10% was obtained depending on $Br^-$ concentration. They utilized 5 min irradiations, 5-10 min decay and 5 min counting for $^{80}Br$ at a flux of $2.4 \times 10^{12}$ n $cm^{-2}s^{-1}$, and $Cl^-$ was also determined simultaneously with this scheme. For samples with a very high Na and $Cl^-$ and low $Br^-$ contents, they used an 8 h irradiation under cadmium foil (to reduce $^{24}Na$ production) and a 30 min count of $^{82}Br$ after 65 h decay. Although more time-consuming than the short irradiation scheme, they successfully measured $Br^-$ in Analar NaCl, finding a concentration of 0.026 µg $Br^-$ per mg $Cl^-$ (26 ppm).

In summary, it is clear that INAA with or without sample pretreatment is a highly sensitive technique for $Br^-$ analysis in waters. Many of the problems inherent in applying other techniques to often highly polluted road runoff samples are eliminated, and although problems of a different nature can arise, such as interference from background $^{24}Na$, careful application of appropriate irradiation, decay and counting schemes can frequently reduce or eliminate many of these.

### 4.1.2 Neutron Activation Analysis of Solid Environmental Samples

The types of solid sample collected during this work for which Br and Cl analysis was required were air filters, suspended solids, road dust, tyre rubber and bitumen.

X-ray fluorescence (XRF) and INAA are by far the most common methods of air filter elemental analysis for Br and Cl reported in the literature. Harrison and Sturges (1983) in their review of the literature on Br/Pb ratios in air cite Br concentrations fom 31 papers; ten of these utilised INAA for Br analysis and fourteen XRF. Giauque *et al.* (1974) and O'Connor *et al.* (1978) outlined the main advantages of the XRF technique for air filter analysis compared with other (non-nuclear) techniques; and those shared by INAA are:-

(i) Highly sensitive, multielement technique

(ii) No filter pretreatment necessary

(iii) Matrix effects are negligible

(iv) Non-destructive technique allows repeat measurements

(v) Only a portion of the filter is required for analysis, allowing other analyses to be carried out on the remainder.

Rapidity of INAA analysis compared with XRF must depend to some extent on the concentrations of Br encountered, but generally these will be quite adequate to allow short irradiation and decay times necessary for rapid sample turnover. Advantages of the method compared with XRF are that Br and Cl can easily be determined simultaneously and loss of these elements during irradiation does not occur.

Dams et al. (1970) undertook a wide investigation of elemental concentrations in air in industrial areas of Indiana, USA and quoted detection limits (from 24 h sampling runs) of 0.004 $\mu g\ m^{-3}$ and 0.1 $\mu g\ m^{-3}$ for Br and Cl respectively, and this is typical of the sensitivity range available with this technique. Relative standard deviations of 9.6% for Br at 0.083 $\mu gm^{-3}$ and 30.3% for Cl at 0.76 $\mu g\ m^{-3}$ were quoted for INAA analysis of these elements in a study of air quality in a road tunnel by Ondov et al. (1982). Other recent applications of the technique in this area are those of Crecelius et al. (1980), Khandekar et al. (1982) and Kowalczyk et al. (1982).

Bromine and Cl in suspended solids from aqueous samples have been determined using INAA by Nadkarni and Morrison (1978) and Ellis and Chattopadhyay (1979) among others. The former authors noted that from a review of 21 published studies on analysis of trace elements in various sediments, the analytical techniques were confined to either atomic absorption spectrophotometry (AAS) (for metals) or NAA, with only one use of XRF reported. They reported a precision of within ±10% for their own work on 100-400 mg samples of lake sediments, which included samples with Br contents in the range 23-96 mg $kg^{-1}$ and Cl 20-609 mg $kg^{-1}$. Ellis and Chattopadhyay (op. cit.) utilised various irradiation and decay schemes for analysing 28 elements in estuarine suspended matter, and reported precisions in the range ±10-16%. Their analyses of standard reference materials were within ±10% of the given values. For Br, concentrations fell in the range 0.27-4.7 mg $kg^{-1}$ and for Cl, 0.12-6.4 mg $kg^{-1}$.

The work of Farmer and Cross (1978) is of particular relevance to the present work, since they analysed a range of Glasgow soil

samples and street dusts for Pb (by AAS) and Br (by INAA) to study the movement of Br relative to Pb in the soil. A long (24 h) irradiation was used on 20 mg samples, and the $^{82}Br$ isotope was counted after 7 days decay. Triplicate analyses gave a typical relative standard deviation of ±20% in a concentration range of 4-56 mg $kg^{-1}$. Hopke et al. (1980) also analysed street dusts from Urbana, Ill., USA, for Br as part of a wider survey, and quoted a mean concentration of 84 mg $kg^{-1}$, very similar to the range found by Farmer and Cross. No further details of precision etc. were given, however. Chlorine was not determined in either of these two studies.

Very few trace analyses of Br and Cl in tyre rubber and bitumen have been reported, but INAA has been used for Zn in tyre rubber (Christensen and Guinn, 1979) and for a wide range of trace elements, incuding Br and Cl, in samples of various crude oils (e.g. Filby and Shah, 1975; Shaw et al., 1981). Crude oil is in many ways a similar sample matrix to bitumen. Filby and Shah (op. cit.) reported a detection limit of 1.5 ng $g^{-1}$ for Br and 10 ng $g^{-1}$ for Cl. In replicate determinations in fuel oil, nine Br determinations gave an RSD of 13.6% at 39.1 ppb, and eight Cl determinations an RSD of 6.5% at 7.8 ppb. Comparisons with National Bureau of Standards reference methods were satisfactory.

In conclusion, work reported in the literature confirms that INAA is more generally applicable to Br and Cl analysis in the variety of solid samples of interest in the present work than any comparable technique, such as XRF. For halide analysis in such samples as road dust and tyre rubber, it is probable that any other technique apart from a nuclear method would be extremely difficult to apply satisfactorily.

## 4.2 Evaluation of Neutron Activation Analysis of Runoff Samples

### 4.2.1 General

Use of INAA techniques for $Br^-$ analysis in river waters, tap water and some sewage effluent samples was extensively evaluated by Luong (1983), using the same facilities and general techniques as in the present work. The method was found to be satisfactory and comparable with a standard chemical method for $Br^-$ analysis in water samples (American Society for Testing and Materials, 1977). In view

of this evaluation of the method for the present work was restricted to $Br^-$ recovery experiments with motorway runoff samples covering a range of $Br^-$ concentrations. Recoveries for $Cl^-$ were also examined.

### 4.2.2 Experimental

Bromide and $Cl^-$ recovery experiments were undertaken on a range of eight runoff samples. Original sample $Br^-$ concentrations ranged from 0.08 to 3.1 $mgl^{-1}$, $Cl^-$ from 1.7 to 41 $mgl^{-1}$. Samples were spiked with $Br^-$ (as KBr) and $Cl^-$ (as KCl) giving, for all eight samples, overall $Br^-$ and $Cl^-$ concentration range of 0.08 to 6.4 $mgl^{-1}$ and 1.7 to 89 $mgl^{-1}$ respectively. For each sample, eight unfiltered subsamples of nominal volume 40 ml were measured using 100 ml measuring cylinders into beakers suitable for freeze drying (section 3.9.1(c)). Volumes were determined accurately by weighing of beakers plus sample to ±0.01 g. One pair of subsamples were unspiked, the remainder spiked in pairs to give a range of $Br^-$ and $Cl^-$ concentrations as given in Table 4.1 and 4.2 respectively. All samples were then frozen, freeze dried, pelleted and analysed by INAA according to the procedures described in section 3.9.1. Linear regression analysis was applied to the data to give the best fit between values of "found" and "added" concentrations. Recoveries were calculated based on the x-axis intercept value (i.e. "found" concentration = 0) derived from the regression equation. Tables 4.1 and 4.2 present the recovery data for $Br^-$ and $Cl^-$ respectively.

### 4.2.3 Results and Discussion

From Table 4.1 it can be seen that percentage $Br^-$ recoveries were, with the exception of sample 8 (84.4%), generally satisfactory, ranging between 96.1 and 109% for the remaining seven samples. The mean of all eight means is 99.0%. The percentage variation about the mean concentration of unspiked samples is 3% or less, except for sample 2 (±12%). Within the range of $Cl^-$ concentrations (spiked and unspiked) found in samples 1-7 (1.7 to 49.6 $mgl^{-1}$) there is no significant effect of increasing $Cl^-$ concentration on $Br^-$ recovery.

Chloride recoveries (Table 4.2) show a slightly wider range than $Br^-$ (95.8-113% for samples 1-7, sample 8, 81.8%). The mean of mean recoveries is 99.7%. Percentage variation about unspiked sample concentration means is ±6.4% or less.

TABLE 4.1 : Results of INAA bromide recovery experiments

| Sample 1 | | | Sample 2 | | | Sample 3 | | | Sample 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) |
| (Intercept value** = 0.083) | | | (Intercept value** = 0.113) | | | (Intercept value** = 0.297) | | | (Intercept value** = 0.587) | | |
| 0.0 | 0.083 | 100.0 | 0.0 | 0.139 | 123.0 | 0.0 | 0.278 | 93.6 | 0.0 | 0.549 | 93.5 |
| 0.0 | 0.087 | 104.8 | 0.0 | 0.109 | 96.5 | 0.0 | 0.287 | 96.6 | 0.0 | 0.572 | 97.4 |
| 0.051 | 0.148 | 110.4 | 0.128 | 0.251 | 104.1 | 0.229 | 0.534 | 101.5 | 0.253 | 0.884 | 105.2 |
| 0.051 | 0.120 | 89.6 | 0.127 | 0.264 | 110.0 | 0.229 | 0.477 | 90.7 | 0.252 | 0.848 | 101.1 |
| 0.102 | 0.188 | 101.6 | 0.256 | 0.397 | 107.6 | 0.459 | 0.792 | 104.8 | 0.761 | 1.347 | 99.9 |
| 0.101 | 0.196 | 106.5 | 0.253 | 0.403 | 111.4 | 0.456 | 0.684 | 90.8 | 0.758 | 1.294 | 96.2 |
| 0.153 | 0.251 | 106.3 | 0.381 | 0.541 | 109.5 | 0.679 | 0.979 | 99.4 | 1.144 | 1.722 | 99.5 |
| 0.153 | 0.226 | 95.8 | 0.380 | 0.527 | 106.9 | 0.689 | 0.902 | 91.5 | 1.140 | 1.712 | 99.1 |
| | Mean | 101.9 | | Mean | 108.6 | | Mean | 96.1 | | Mean | 99.0 |
| | RSD | 6.6% | | RSD | 6.9% | | RSD | 5.6% | | RSD | 3.5% |
| Sample 5 | | | Sample 6 | | | Sample 7 | | | Sample 8 | | |
| $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Br^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) |
| (Intercept value** = 0.793) | | | (Intercept value** = 0.901) | | | (Intercept value** = 1.478) | | | (Intercept value** = 3.734) | | |
| 0.0 | 0.766 | 95.9 | 0.0 | 0.872 | 96.8 | 0.0 | 1.500 | 101.5 | 0.0 | 3.090 | 82.8 |
| 0.0 | 0.808 | 101.1 | 0.0 | 0.911 | 101.1 | 0.0 | 1.517 | 102.6 | 0.0 | 3.073 | 82.8 |
| 0.758 | 1.554 | 99.8 | 0.630 | 1.565 | 102.1 | 0.756 | 2.163 | 96.8 | 1.277 | 4.427 | 88.3 |
| 0.761 | 1.629 | 104.4 | 0.631 | 1.553 | 101.4 | 0.763 | 2.155 | 96.2 | 1.293 | 4.196 | 83.5 |
| 1.498 | 2.591 | 112.8 | 1.247 | 2.160 | 100.6 | 1.535 | 2.858 | 94.9 | 2.564 | 5.353 | 85.0 |
| 1.514 | 2.327 | 100.6 | 1.239 | 2.139 | 100.0 | 1.524 | 3.192 | 106.3 | 2.557 | 5.431 | 86.3 |
| 2.267 | 3.218 | 105.0 | 1.894 | 2.921 | 104.5 | 2.274 | 3.851 | 102.6 | 3.867 | 6.415 | 84.4 |
| 2.221 | 3.125 | 97.0 | 1.882 | 2.666 | 95.8 | 2.301 | 3.662 | 96.9 | 3.851 | 6.266 | 82.6 |
| | Mean | 102.1 | | Mean | 100.3 | | Mean | 99.7 | | Mean | 84.4 |
| | RSD | 5.3% | | RSD | 2.8% | | RSD | 4.1% | | RSD | 2.4% |

** Intercept value = intercept on x-axis derived from regression equation

* Recovery (%) = found concn x 100/added concn + intercept value

TABLE 4.2 : Results of INAA Chloride recovery experiments

| Sample 1 | | | Sample 2 | | | Sample 3 | | | Sample 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) |
| (Intercept value** = 1.58) | | | (Intercept value** = 1.70) | | | (Intercept value** = 5.29) | | | (Intercept value** = 8.04) | | |
| 0.0 | 1.81 | 114.6 | 0.0 | 1.85 | 108.8 | 0.0 | 4.65 | 87.9 | 0.0 | 8.17 | 101.6 |
| 0.0 | 1.73 | 109.5 | 0.0 | 2.06 | 121.2 | 0.0 | 5.29 | 100.0 | 0.0 | 7.69 | 95.6 |
| 1.02 | 3.08 | 118.5 | 2.05 | 4.20 | 112.0 | 3.82 | 9.65 | 105.9 | 7.60 | 15.54 | 99.4 |
| 1.02 | 2.81 | 108.1 | 2.02 | 3.98 | 107.0 | 3.82 | 8.27 | 90.8 | 7.57 | 14.54 | 93.1 |
| 2.05 | 4.64 | 127.8 | 4.09 | 6.42 | 110.9 | 7.65 | 12.53 | 96.8 | 14.99 | 22.34 | 97.0 |
| 2.03 | 3.53 | 97.8 | 4.06 | 6.63 | 115.1 | 7.59 | 12.01 | 93.2 | 14.92 | 21.75 | 94.7 |
| 3.06 | 5.52 | 119.0 | 6.09 | 8.62 | 110.7 | 11.47 | 16.81 | 100.3 | 22.63 | 30.15 | 98.3 |
| 3.05 | 4.92 | 106.0 | 6.08 | 8.86 | 113.9 | 11.49 | 15.38 | 91.7 | 34.98 | 41.67 | 96.9 |
| | Mean | 112.7 | | Mean | 112.5 | | Mean | 95.8 | | Mean | 97.1 |
| | RSD | 8.2% | | RSD | 3.9% | | RSD | 6.3% | | RSD | 2.8% |
| Sample 5 | | | Sample 6 | | | Sample 7 | | | Sample 8 | | |
| $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) | $Cl^-$ concn ($mgl^{-1}$) Added | Found | Recovery* (%) |
| (Intercept value** = 12.82) | | | (Intercept value** = 14.14) | | | (Intercept value** = 19.64) | | | (Intercept value** = 51.54) | | |
| 0.0 | 13.14 | 102.5 | 0.0 | 13.41 | 94.8 | 0.0 | 20.35 | 103.6 | 0.0 | 41.26 | 80.1 |
| 0.0 | 13.65 | 106.5 | 0.0 | 14.63 | 103.5 | 0.0 | 20.22 | 103.0 | 0.0 | 41.24 | 80.0 |
| 10.11 | 22.21 | 96.9 | 10.08 | 24.36 | 100.6 | 10.08 | 29.20 | 98.3 | 18.66 | 57.68 | 82.2 |
| 10.15 | 22.32 | 97.2 | 10.09 | 23.41 | 96.6 | 10.18 | 26.60 | 89.2 | 18.90 | 58.01 | 82.4 |
| 19.97 | 33.83 | 103.2 | 20.09 | 32.93 | 96.2 | 19.97 | 39.02 | 98.5 | 36.98 | 74.57 | 84.2 |
| 20.19 | 32.55 | 98.6 | 19.95 | 32.47 | 95.2 | 19.83 | 39.15 | 99.2 | 36.88 | 75.05 | 84.9 |
| 30.23 | 44.17 | 102.6 | 30.20 | 44.60 | 100.6 | 29.35 | 49.57 | 101.2 | 56.03 | 89.35 | 83.1 |
| 32.28 | 44.98 | 99.7 | 30.01 | 43.03 | 97.5 | 29.71 | 48.27 | 97.8 | 55.80 | 83.33 | 77.6 |
| | Mean | 100.9 | | Mean | 98.1 | | Mean | 98.9 | | Mean | 81.8 |
| | RSD | 3.3% | | RSD | 3.2% | | RSD | 4.5% | | RSD | 2.9% |

** Intercept value = intercept on x-axis derived from regression equation
* Recovery (%) = found concn x 100/added concn + intercept value

Few data are available in the literature concerning INAA $Br^-$ and $Cl^-$ analyses of runoff samples to permit comparison of this data with that of others. For tap water samples, however, Luong (1983) reported a mean $Br^-$ recovery of 100.1% from three samples of tap water, and 99.6% for two samples of upland surface water, and values from the present work are comparable with these data. Reproduceabilites are generally better than those reported by Habib and Minski (1981) for river water. Chloride recoveries were not examined, and in general INAA does not appear to be widely used for $Cl^-$ determination in aqueous environmental samples. This is chiefly because the technique is applied mainly to trace element analysis which frequently requires irradiation/decay schemes which are not convenient for $Cl^-$ analysis, which can in any case usually be determined easily by other means at the concentrations normally found.

As referred to in section 3.9.1(a), samples containing higher levels of sodium chloride (usually $\gtrsim$~100 $mgl^{-1}$ as $Cl^-$) cannot be analysed for $Br^-$ using the short irradiation/decay scheme because of high initial Na activity ($\frac{1}{2}$ life 15h). The long irradiation procedure previously described was used for these samples. Since the sample preparation techniques and basic modes of analysis are identical to those used for short irradiations, no separate recovery experiments were carried out. Luong (1983), however, reported very good $Br^-$ recovery efficiencies (102%±0.98% from sodium chloride solutions) using identical techniques and equipment to that in this work. This was attributed to greater precision and lower detection limits arising from long irradiation and counting times.

## 4.3. Solid Sample Analysis

Analysis for Br and Cl by INAA was also applied to a limited number of air filters, suspended solids, road dust, tyre rubber and bitumen samples, since, with suitable changes in sample preparation (section 3.9.2), the identical basic INAA technique and equipment could be easily utilised. The method has been successfully applied by other workers for air filters (e.g. Winchester *et al.*, 1967; Martens *et al.*, 1973), suspended solids and similar materials (Nadkarni and Morrison, 1978; Ellis and Chattopadhyay, 1979), so separate recovery tests for these samples were not carried out, especially in view of

the difficulties in ensuring complete homogeneity in solid samples necessary for extensive recovery tests. Validation of the method in the literature has usually relied upon comparative analyses using other techniques such as XRF (e.g. Martens et al., 1973).

# SECTION 5 . CHARACTERISTICS OF UNTREATED MOTORWAY RUNOFF - RESULTS AND DISCUSSION

## 5.1 Introduction

The examination of untreated runoff (UTR) quality presented in this section follows a sequential pattern. Firstly, data concerning the hydrology and prevailing environment of the catchment is presented, in order to provide a setting for the presentation of runoff quality data which follows. This second section provides a review of runoff quality as examined during the entire sampling period, November 1980 - September 1981. Possible sources of the contaminants are discussed and the major factors affecting their concentrations in runoff are also considered. The third section comprises a more formal statistical analysis of the factors affecting runoff loadings of some of the parameters examined, based on the trends evident in the preceding section.

## 5.2 Catchment Hydrology and Environment

### 5.2.1 Data Analysis

Statistical tests have been employed to examine differences between the means of parameters. Most of the common statistical tests (for example, student's t-test) are based on the assumption that the data are normally distributed. There is, however, one important case where it is permissible to make use of such an assumption even though the observations may have arisen from some other distribution; that is when dealing with the sample mean (Ellis and Lacey, 1980). It has been noted that with almost any original distribution, the distribution of the sample mean tends rapidly to the normal as the sample size increases (Davies and Goldsmith, 1977). For these reasons, the t-test has generally been applied to establish if the differences between means of parameters of interest are real and not have arisen by chance. In cases where there have been doubts as to its applicability a distribution-free test (Rank Sum Test; Davies and Goldsmith, op. cit.) has been employed as a check.

### 5.2.2 Catchment Hydrology

#### (a) Rainfall Distribution in the Site Area

The only source of continuous rainfall data in the site area was a Meteorological Office rain gauge located 3.2 km SW of the site at Dunstable Cement Works. Annual average rainfall at this site is 648 mm (Meteorological Office, 1980). Runoff sampling took place at the site intermittently between 2 November 1980 and 3 October 1981 (designated as weeks 1-48). Weekly rainfall totals for this period as measured at the Dunstable gauge are shown in Fig. 5.1. Totals for weeks 4, 10, 11, 17 and 26 included snowfall. During this period total rainfall was 530.6 mm. For the closely corresponding period 1 November 1980 - 30 September 1981 total rainfall was 530.6 mm, representing 90% of the long-term average for these months. The shortfall was accounted for mainly during the months November-March, when total rainfall was 71% of average. Rainfall for April to September was 106% of average. For reasons discussed in section 5.2.4, the overall sampling period has been divided into "winter" and "summer" periods, "winter" being defined as 2 November 1980 - 28 March 1981 (weeks 1-21) and "summer" as 29 March 1981 - 3 October 1981 (weeks 22-48).

#### (b) General Hydrological Characteristics of Runoff Events

Total runoff volumes (rain and snowfall) from catchment A monitored during the study period are shown in Fig. 5.2. For some weeks complete flow data were not available due mainly to instrumental failure. Where possible, data from sedimentation tank records (catchment B) have been substituted, since flow values and volumes were generally within ±10% for the two catchments (Ofori, 1984a). Where complete flow data from neither catchment A nor B were available, this is indicated in Fig. 5.2. Figures 5.3 and 5.4 present maximum peak flows and maximum mean flows per week for the same period. Indication is made on the figures where these maxima arise from snowfall events. The total flow for weeks when full flow records were available (weeks 1-48 excluding 5, 6, 29, 36) was 322000 l.

Excluding periods when no flow record was available from catchment A, a total of 181 events were monitored for flow, about 90% of the total. Volumes smaller than 50 l cannot be realistically measured, but the number of event volumes below this value is con-

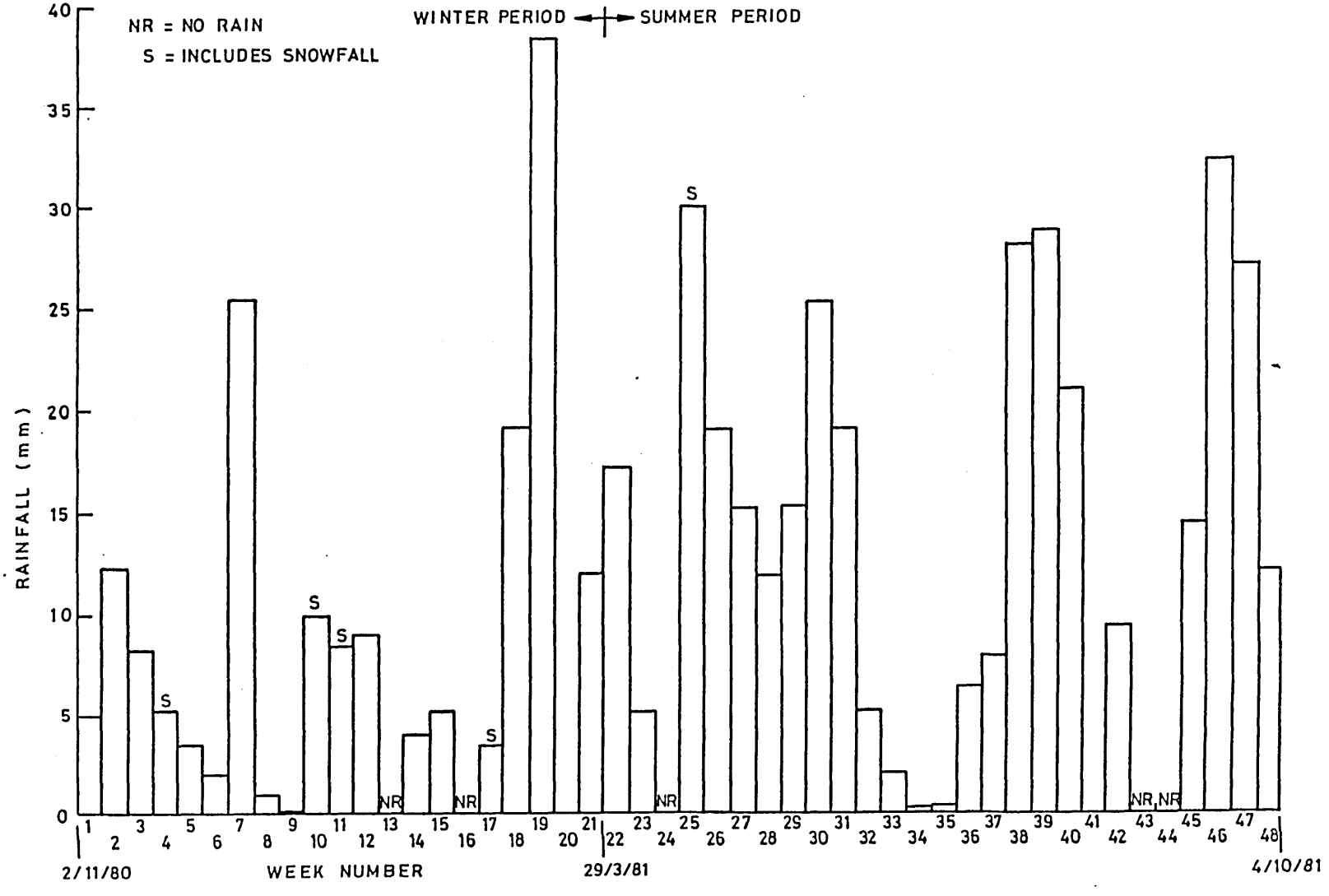



Figure 5.1 Weekly rainfall totals

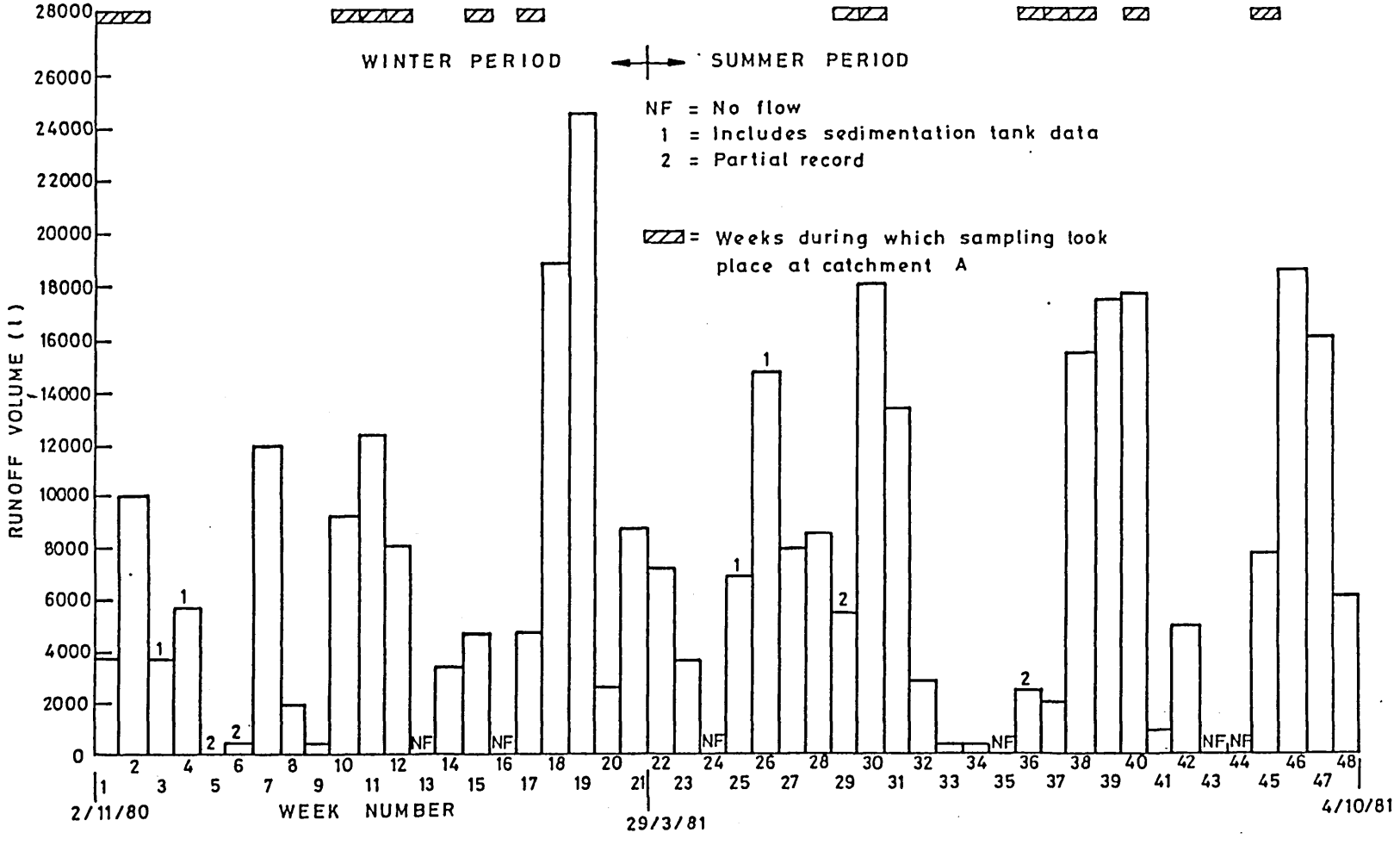



Figure 5.2 Weekly runoff volume totals

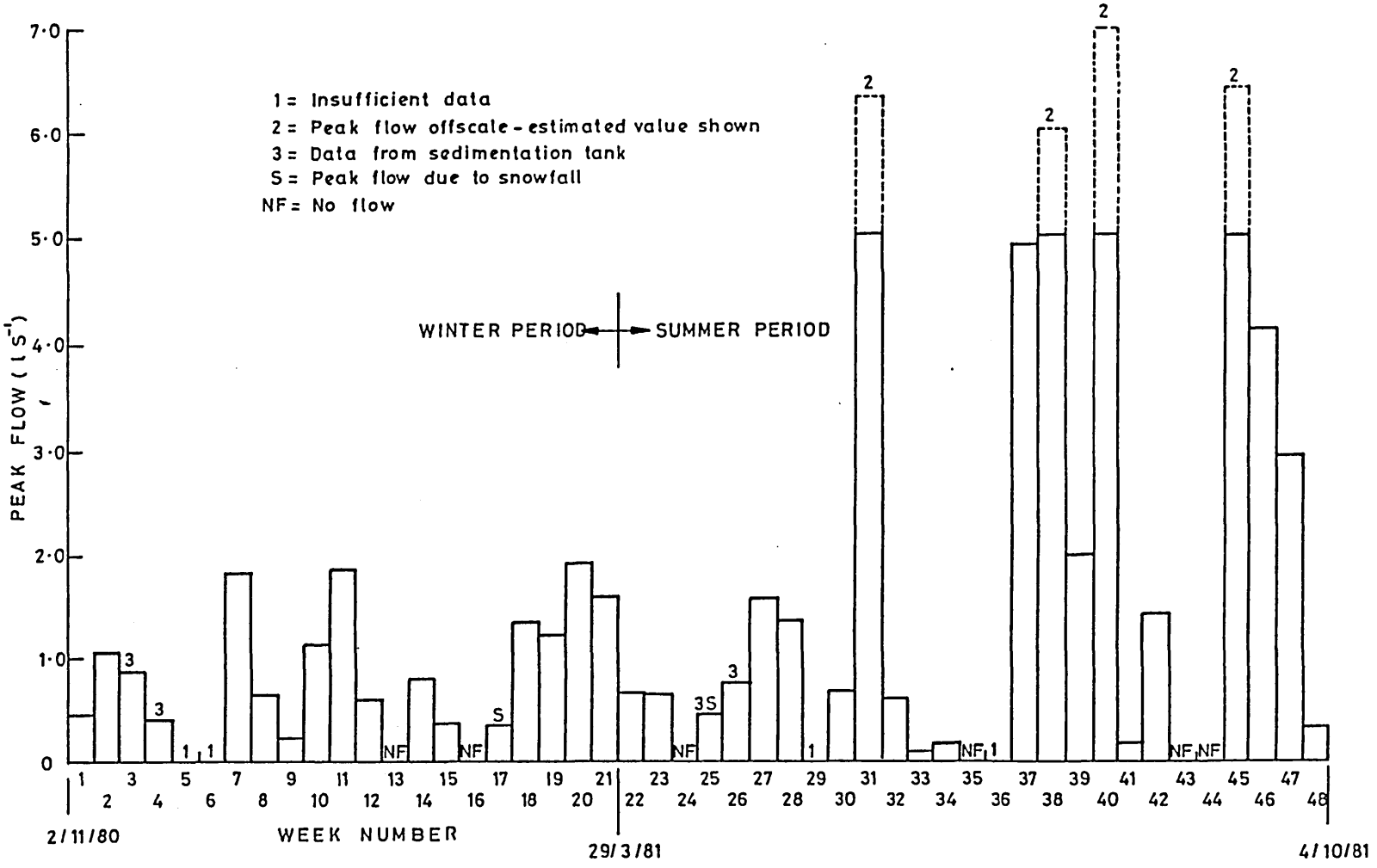



Figure 5.3 Weekly peak flows

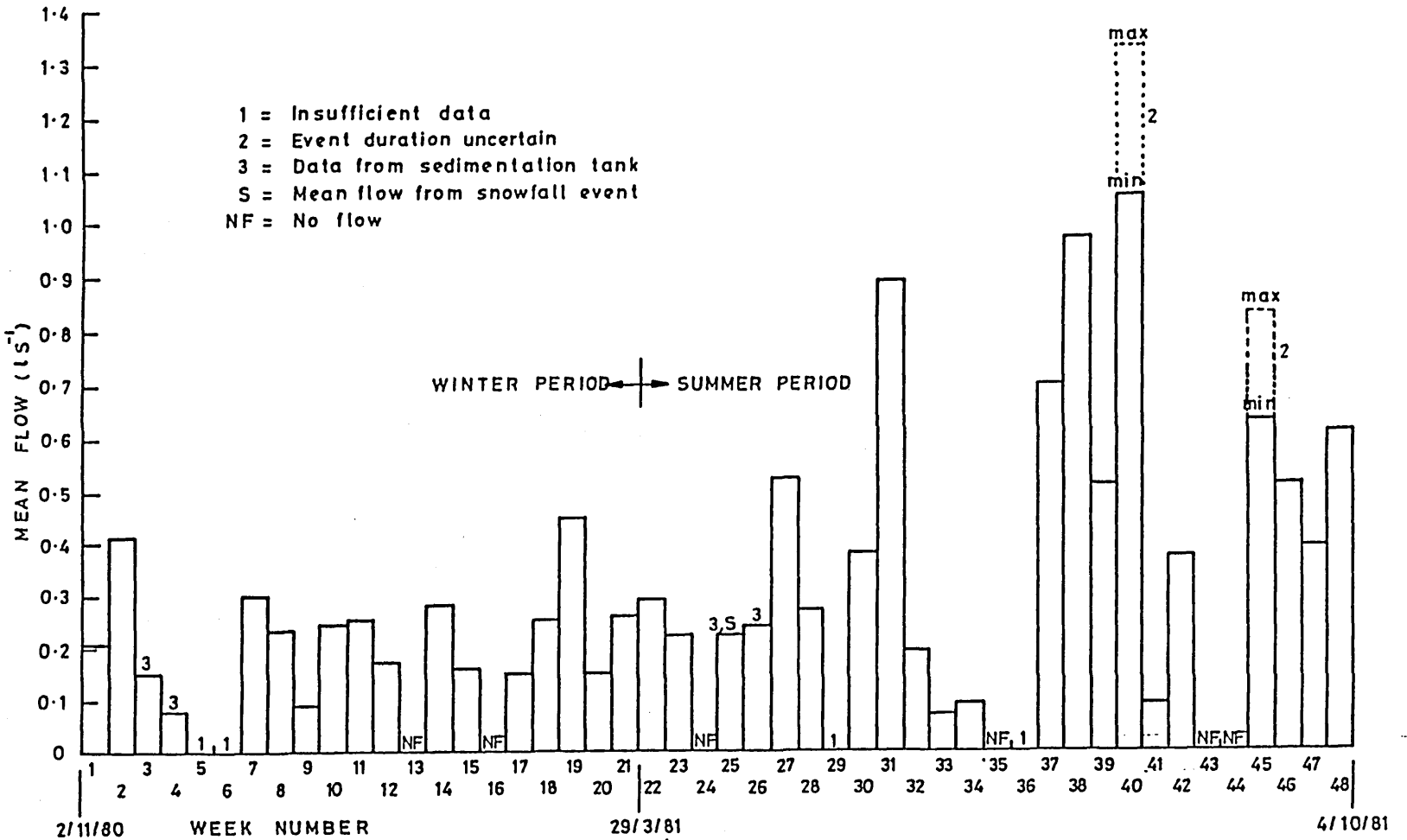



Figure 5.4 Weekly maximum mean flows.

sidered to be extremely small. The basic statistics for event volumes and mean flows are summarised in Table 5.1 and Figures 5.5 and 5.6.

TABLE 5.1 : Statistical data for volumes and mean flows for 181 events measured at catchment A

| Parameter | Percentiles | | | Means | | SD | Range |
|---|---|---|---|---|---|---|---|
| | 5 | 50 | 95 | G* | A** | | |
| Volume (l) | 158 | 912 | 5623 | 853 | 1627 | 2265 | 50-17050 |
| Mean Flow ($ls^{-1}$) | 0.06 | 0.13 | 0.52 | 0.15 | 0.19 | 0.17 | 0.05-1.20 |

* Geometric; ** Arithmetic; SD = Standard Deviation

Inspection of the 5, 50 and 95 percentile values and range figures in the Table 5.1 reveals that both basic distributions are highly skewed towards lower values, 50% of volumes and mean flows being less than 912 l and 0.13 $ls^{-1}$ respectively. This clearly reflects the relative scarcity of prolonged, high intensity events in the prevailing hydrological regime in the site area.

Seasonal changes in prevailing rain intensities and resultant runoff flows are indicated by the trend towards higher peak and mean flows during the summer period (Figures 5.3 and 5.4), when convective storms probably contribute a greater number of short, relatively intense events to the overall event population than in winter. The trend to bimodality in the mean flow histogram of Fig. 5.6 is probably an indication of this trend, which is also apparent in that the upper four classes of the distribution are occupied by summer events (hatched area). In contrast, the volume histogram shows a distribution nearer log normality, and the contribution from summer events is not so predominant in the upper four classes as with mean flows, indicating that changes in intensity do not necessarily entail greater event volumes. It should be noted that the number of events included from the winter and summer periods in Figures 5.5 and 5.6 are 91 and 90 respectively, so that the contribution to histogram areas of summer events reflects underlying trends, not differences in population size.

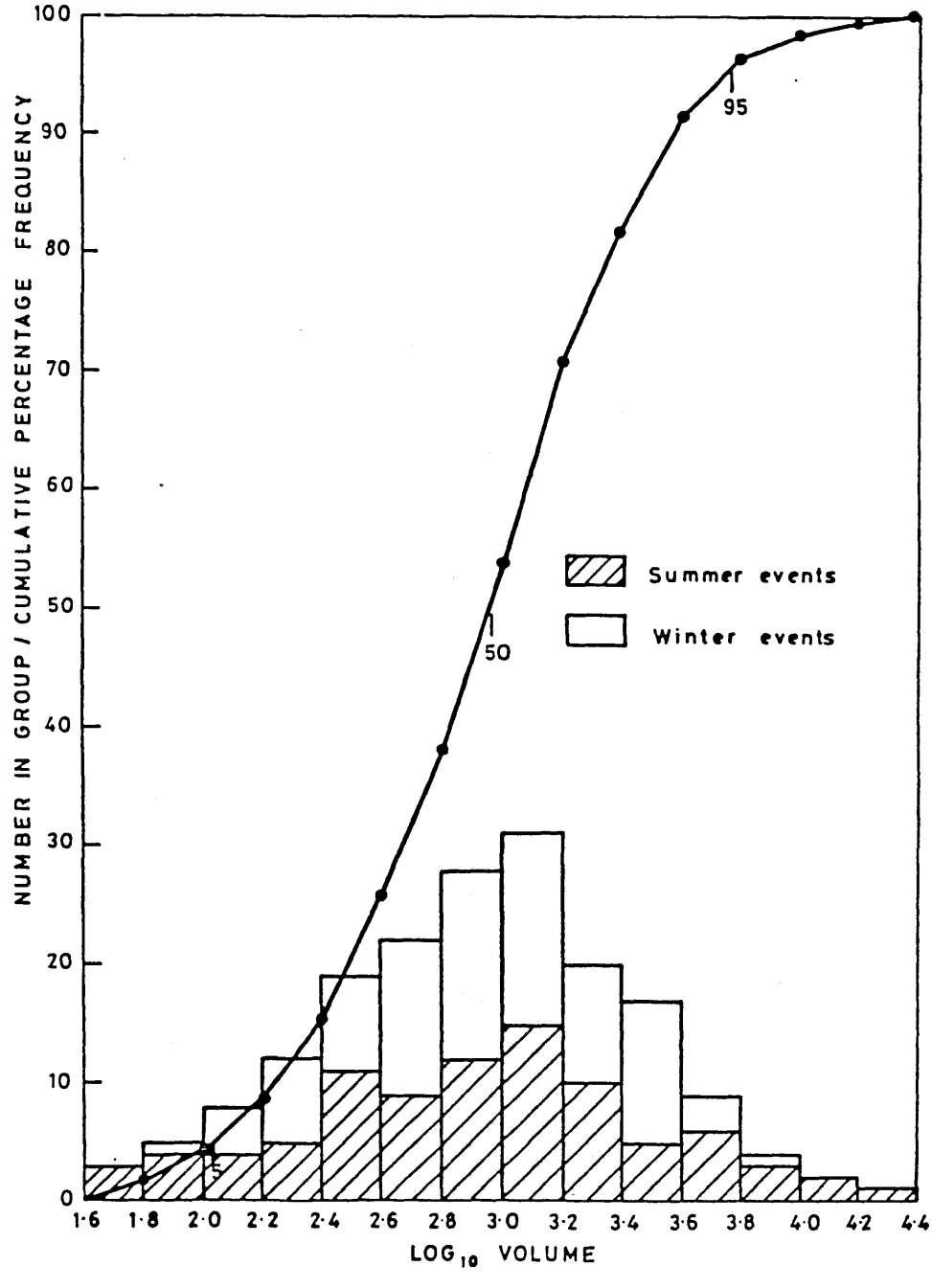



Figure 5.5 Histogram of event volume data

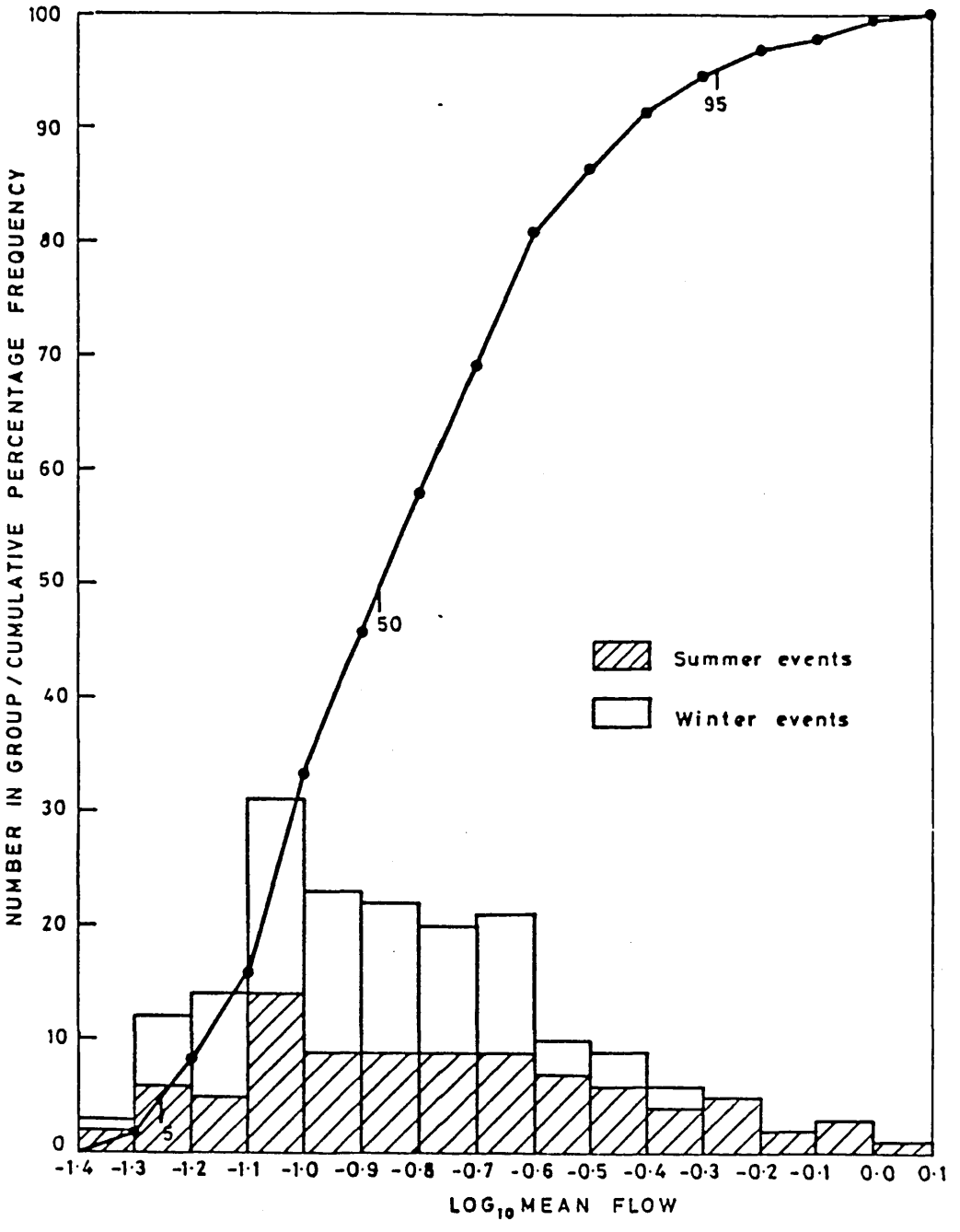



Figure 5.6 Histogram of event mean flow data

(c) Hydrological Characteristics of Sampled Events

Twenty five events were sampled, thirteen in winter and twelve in summer. The weeks during which sampling took place are shown in Fig. 5.2. Table 5.2 presents a summary of the events sampled in terms of volume, peak flow, mean flow, peak/mean ratio, duration and rise time, this last term being defined as the time in hours from the start of runoff to the peak flow.

The trend to higher peak flows and mean flows in summer which is evident in Figures 5.3 and 5.4 is clearly reflected in the differences between the respective means in the table, and both these differences are significant at $P > 0.95$. Volumes also show a slight trend to higher summer values, although this is not statistically significant. Summer means for peak/mean ratios, event durations and rise time are all significantly greater than winter means at $P > 0.95$ ($> 0.98$ for duration), and these results are complementary aspects of the basic differences between winter and summer events which are clear from the table as a whole. The high RSD values for many of the parameters show, however, that the range of the data is frequently very wide.

(d) Rainfall-Runoff Relationships

Comparison of Figs. 5.1 and 5.2 show that, as expected, the underlying pattern in the rainfall and runoff volume data is similar, and the correlation coefficient between the weekly runoff and rainfall totals is 0.90. A detailed comparison between rainfall measured at the Dunstable gauge and that falling at the site itself was made by Ofori (1984a) who, applying the standard t-test technique, found that the mean of the same 22 daily rainfall totals measured at both sites only differed by 8% and were not significantly different at the $P > 0.9$ confidence level. It was considered legitimate, therefore, to use the Dunstable weekly totals to estimate an overall runoff coefficient for the catchment. Excluding weeks 5, 6, 29 and 36 (incomplete flow records), the total event volume and rainfall figures were 322218 l and 508.0 mm respectively. The total volume given is equivalent to 405.9 mm effective rainfall over the catchment; thus the runoff coefficient is 0.80. For comparison, Klein (1982) reports coefficients of 0.92 and 0.72 for two impermeable motorway surfaces in West Germany,

TABLE 5.2 : Hydrological characteristics of sampled events

| | Volume (l) | Peak Flow ($ls^{-1}$) | Mean Flow ($ls^{-1}$) | Peak/Mean | Duration (h) | Rise Time (h) |
|---|---|---|---|---|---|---|
| WINTER (n = 13) | | | | | | |
| Mean | 2515 | 0.40 | 0.16 | 2.36 | 4.03 | 1.67 |
| RSD (%) | 75 | 65 | 56 | 28 | 60 | 93 |
| Range | 221-6336 | 0.10-1.04 | 0.07-0.24 | 1.3-3.44 | 0.85-10.33 | 0.15-4.32 |
| SUMMER (n = 12) | | | | | | |
| Mean | 3154 | 2.14 | 0.41 | 4.0 | 1.95 | 0.47 |
| RSD (%) | 129 | 116 | 80 | 58 | 0.56 | 1.42 |
| Range | 220-14720 | 0.09-~7.0[a] | 0.07-~1.2[b] | 1.29-~8.77[a] | 0.71-3.48 | 0.09-2.48 |
| Significance levels of differences between means | <0.9 | >0.95 | >0.95 | >0.95 | >0.98 | >0.95 |

RSD = Relative Standard Deviation

[a] = peak flow off scale - estimated value

[b] = event duration uncertain - value ± 0.1 $ls^{-1}$

Cathelain et al. (1981) report a mean value of 0.58 for 86 events from a motorway study site in France, and the FHWA (1981c) a value of 0.87 for a 100% paved highway surface in America. The value of 0.80 found at this site thus appears to fall within the expected range for this type of catchment.

Losses incurred in the rainfall-runoff process are generally due to spray, depression storage, infiltration, evaporation and surface wetting. A separate study of the topic at the site (Bufill, 1981) has shown that about 0.7 mm of rain is lost during any storm, mainly due to surface wetting. Spray was found to be variable source of loss, but its average contribution to losses was less than 8% of total rainfall.

Application of the runoff coefficient value of 0.80 derived above to the total volumes of events sampled (70550 l) indicates that, including losses, this was equivalent to 111.1 mm (21%) of recorded rainfall during the study period. The number of events sampled was about 12% of the total number (~200) occurring during the study period.

### 5.2.3 Catchment Environment

#### (a) Traffic Flow

Total weekly traffic flow during the study period is shown in Fig. 5.7. All data has been taken from the Friars Wash loop (see section 2.5.5) since the Newport Pagnell loop was subject to a series of malfunctions during the same period. Traffic at the site was estimated by taking the mean of the two figures. Since traffic flows at Newport Pagnell were in the region of 75% of those at Friars Wash, sites flows may be taken as approximately 12% less than those shown. Flows during weeks 8 and 9 (21 December - 3 January) were clearly exceptionally low due to the Christmas and New Year holidays. Excluding these two weeks, the mean weekly total flow for the winter period was 251220 vehicles (n = 19, RSD = 3.2%) and for summer 262820 (n = 27, RSD = 3.2%), the summer mean thus being 11,600 (4.6%) greater than that of winter. This difference is statistically significant at the $p > 0.99$ level, but its magnitude would suggest that its importance was probably not very great in environmental terms over the whole year. The difference was presumably due to holiday traffic

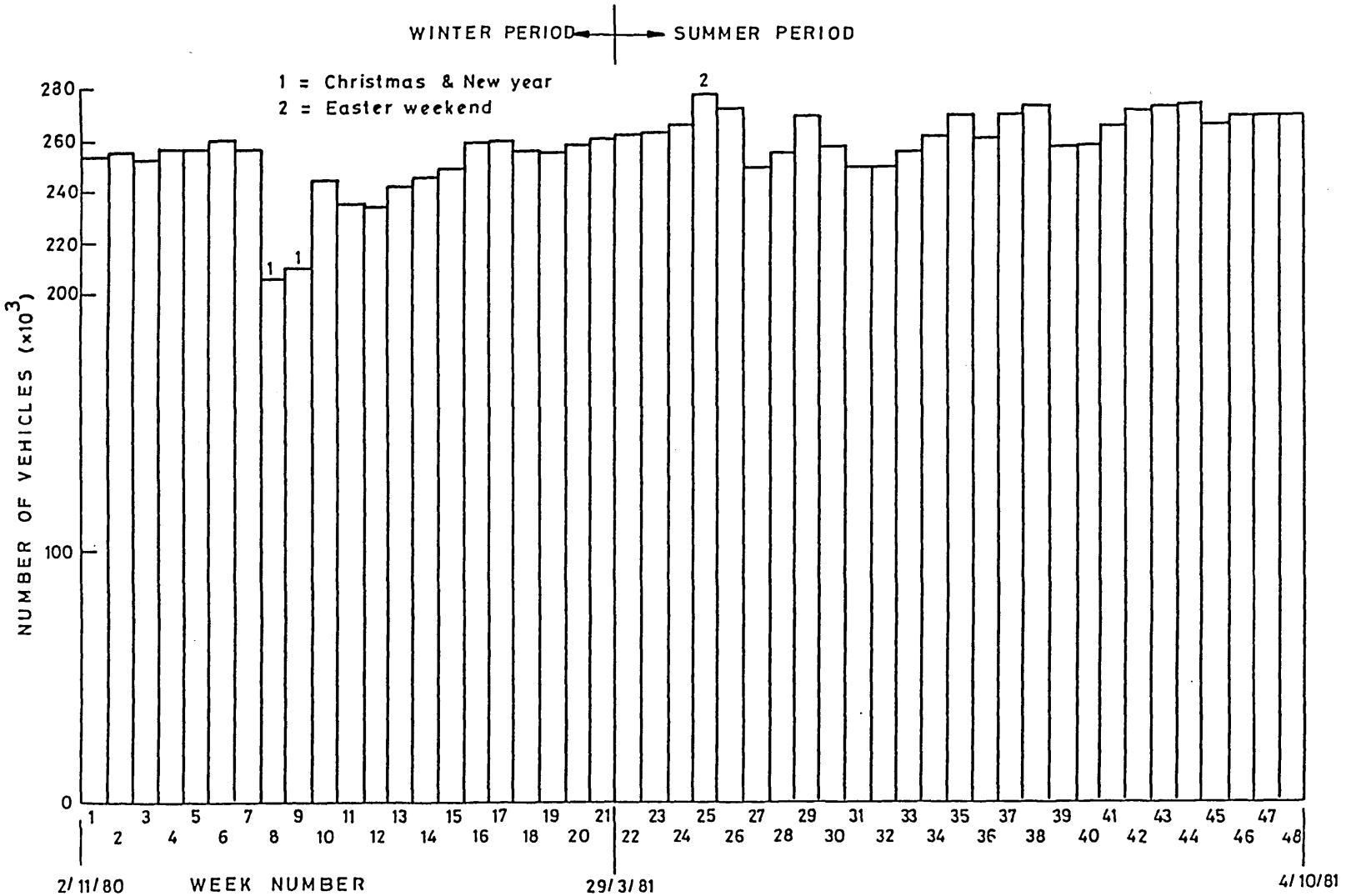



Figure 5.7 Weekly traffic flow data

during the summer months. No sampling took place during the Christmas and New Year periods.

Typical weekday traffic composition figures were: heavy vehicles (over 1525 kg unladen weight) and coaches 26%, light goods 7%, cars and motorcycles 67% (Dove, 1982). There was no evidence of major long term changes in traffic composition during the sampling period (Dove, op. cit.), but there was generally a much lower proportion of heavy goods vehicles making up weekend traffic than during the week.

(b) De-icing Salt Application and Road Sweeping

Apart from traffic, the two other non-hydrological activities most likely to have affected runoff quality were application of de-icing salt and sweeping of the hard shoulders. Figure 5.8 gives data on the distribution of these two activities during the sampling period. It should be noted that salt application rates were calculated from motorway depot records and can only be regarded as approximate. Salt application was clearly one of the most important enviornmental differences between winter and summer periods. The winter of 1980-81 was not particularly severe, a total of 433 tonnes ($\simeq$ 560 $gm^{-2}$) of salt being spread from the Toddington Depot, compared with 982 tonnes during the more severe winter of 1981-82 (Smith, 1982).

Two of the road sweeping runs (weeks 2 and 10) coincided with weeks when sampling was taking place. For these two occasions, the number of days elapsing between the road sweeping day and the next sampled event were four and two respectively. After the sweeping run in week 44, thirteen days elapsed before the next sampled events. In general, however, road sweeping activities were only carried out sporadically, and, on the whole, will not have had a major impact on road surface conditions for most of the sampling period.

5.2.4 Definition of "Winter" and "Summer" Periods

The analysis of runoff quality presented in section 5.5 following shows clearly that several factors which affect quality show significant seasonal variations. Accordingly, it was considered use-

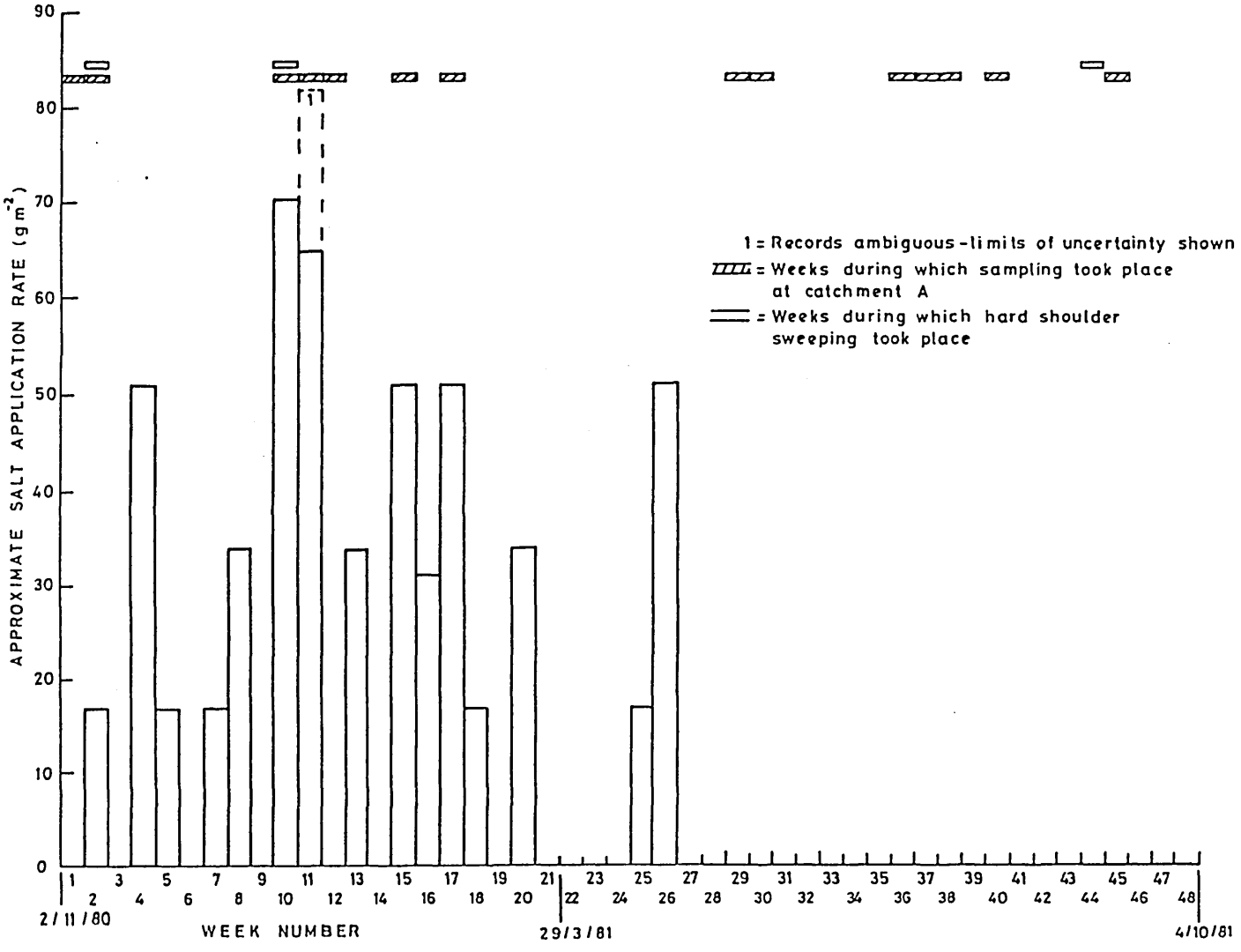



Figure 5.8 Weekly salting and sweeping data

ful to make a broad distinction in terms of "winter" and "summer" between two parts of the sampling period encompassing, as far as possible the chief features of the two periods. The winter period is defined as 2 November 1980 - 28 March 1981 (weeks 1-21) and summer as 29 March - 3 October 1981 (weeks 22-48). It is obviously impossible to define a season in terms of precise dates without some element of arbitrariness, but these periods were chosen because (a) the site was not ready for flow monitoring and sampling of UTR until the beginning of November 1980, so this formed a natural starting point for the winter period; (b) salting on a routine basis has usually ended before 29 March - the application during weeks 25 and 26 was an exceptional occurrence; (c) the convention of classifying winter as 1 November to 31 March for runoff study purposes has been adopted by other authors e.g. Asplund et al. (1982) and the FHWA (1981a).

## 5.3 Runoff and Deposition Sampling and Analysis

### 5.3.1 Sampling and Sample Treatment

Twenty-five events from catchment A were sampled and analysed during the sampling period, thirteen during winter and twelve during summer. Of the thirteen winter period events sampled, eleven were sampled over 65% or more of their volume, while for the twelve sampled in summer, the corresponding figure was ten events. Details of sampling dates, along with hydrological and other pertinent data, are given in Appendix 3. As shown therein, winter events are individually numbered W1-W13 and summer events S1-S12. This designation is used in all subsequent appendices, throughout the remainder of this entire section and in Sections 6, 7, and 8.

The total number of individual samples collected during the entire period was 372. Subjecting these samples to all the analyses for runoff (excluding pH, conductivity, oil and PAH) described in Section 3 (i.e. COD, TS, TVS, TSS, $Cl^-$, Pb, Zn, Cd and $Br^-$) would have required more than 3000 separate analyses. In order to reduce the number to a realistic level, samples from nine of the thirteen winter events were composited on a flow-weighted basis prior to analysis.

This approach was not generally adopted for summer samples for two main reasons. Firstly, compositing samples, although saving a great deal of analytical labour, eliminates many of the data con-

cerning in-storm changes in concentration of the parameters concerned. Secondly, there was a tendency for total suspended solids (TSS) concentrations to be higher in summer events (Section 5.5.4). This led to difficulties in achieving a truly homogeneous distribution of TSS throughout a sample before taking a subsample for compositing, due to very rapid settling of heavier particles. A compromise solution to the problem of excessive analytical work load was therefore adopted. For any specific parameter, samples were analysed on an alternate basis - i.e, where all individual samples for each event were numbered sequentially, even-numbered samples would be analysed for one set of parameters and odd-numbered samples for the remaining parameters. In this way, loadings could still be calculated with a reasonable degree of confidence, while examination of in-storm concentrations was still possible when desired. For two small events with low flows, however, composite samples were still utilised.

In practice, analysis of all events for all parameters on this basis was subject to additional major practical constraints which prevailed throughout the project work. These were:

(a) Frequent but essential site visits and preceding preparation significantly reduced the time available for analytical work in the laboratory.

(b) Maximum sample volume available was 500 ml (single samples) or 1 l (composites). Analyses requiring large sample volumes (e.g. suspended solids) could thus be carried out only for one or two major parameters.

These constraints meant that analyses for one or more parameters were omitted for some events, while lengthy analyses, e.g. for oil and PAH, were restricted to specific sample batches rather than being carried out on a routine basis.

In addition to runoff sampling, five sampling runs for total (wet plus dry) deposition were carried out during the summer period using the grid of gauges on the grass verge at the site and at the farm site, both of which are described in Section 2.5.2. Data concerning length of gauge exposure, rainfall etc., are given in Appendix 4. Sampling was undertaken chiefly as part of the Br work, so samples

were only analysed for a relevant selection of runoff parameters, i.e. pH, EC, TSS, Pb and $Cl^-$ as well as $Br^-$, but concentration data from these gauges have been used for comparative purposes in the discussion of runoff quality in Section 5.5. For one of the sampling periods, no rain occurred, so data from this run have been regarded as dry deposition. Owing to practical constraints, it was not possible to utilise a full set of gauges for all runs, and on one occasion two gauges were vandalised. In all, 22 total deposition and six dry deposition samples from the roadside gauges and four total deposition samples from the farm gauge were analysed.

### 5.3.2 Runoff Data Presentation

Flow-weighted mean (FWM) concentration data for individual events have been used to present overall summaries of sampling period runoff quality for all parameters except pH, EC, oil and PAH. This approach has been adopted in order to take into account variations in flow and concentrations during events which were a major feature of runoff from the site and which are characteristic of stormwater generally. Such variations are not taken into account in measures of contaminant presence such as arithmetic means of individual sample concentrations, and literature which only presents concentrations in this manner is of limited value. The use of FWM values also allows comparison with similar data in other published work, and with statutory limits an effluent concentrations (section 8). For pH and EC, FWM values are not an appropriate measure and have thus been treated on the basic of individual sample data. Oil and PAH were not sampled on an individual event basis and data have thus been presented accordingly (section 5.5.9). Bromide data is presented separately in section 6.

In this work, FWM concentrations are defined as the total load of a parameter removed during sampling, divided by the volume of runoff flowing during sampling. This was derived in one of three ways:

(a) directly from a single event composite sample,

(b) by combining data from two or more composites covering a single event;

(c) by calculating a total load and thus mean concentration from individual sample concentrations and associated volumes.

Event loading data are given in Appendix 5 and FWM data derived from that are given in Appendix 6.

For presentation of FWM data for each parameter in graphical form, FWM values have been ranked in order of increasing magnitude and plotted against concentration. This approach is based upon a method recommended by Davies and Goldsmith (1977), and has been adopted because there are too few individual FWM data to permit construction of meaningful histogram or cumulative frequency curves. Arithmetic means of FWM values for winter and summer respectively (henceforth termed "seasonal means") have been compared on a t-test basis to assess more exactly the extent of any seasonal differences.

## 5.4 Background Deposition Contribution to Runoff Quality

Consideration of runoff quality from any catchment must take into account the contaminant contribution from deposition (wet and dry) when sources of these contaminants are being assessed. Table 5.3 presents a summary of pH, EC, TSS, Pb, $Cl^-$ and $Br^-$ data arising from the deposition sampling (excluding the dry deposition run) undertaken both at the roadside and at the farm site during the present work. Results of statistical comparisons (t-test) between means of roadside and farm data are also given. Bromide data are included in the table for later reference in Section 6.

For TSS and Pb concentration data, the results demonstrate clearly that the proximity of the roadside gauges to the carriageway has a very substantial effect on the amounts of these contaminants being deposited there, while for $Cl^-$, although the effect is not so marked, a trend to lower concentrations in the farm gauges is still evident. Although pH and EC do not, in contrast, show any significant differences between gauge sites, it is in general clearly inappropriate to regard roadside data as an indicator of background concentrations when assessing non-motorway contributions to runoff loads. In the survey of runoff quality which follows, therefore, the farm gauge concentrations of the parameters in Table 5.3 will be regarded as the best available indicator of background concentrations.

TABLE 5.3 : Summary of deposition (wet and dry) data

| | pH | EC ($\mu S\ cm^{-1}$) | TSS ($mgl^{-1}$) | Pb ($mgl^{-1}$) | $Cl^-$ ($mgl^{-1}$) | $Br^-$ ($mgl^{-1}$) |
|---|---|---|---|---|---|---|
| ROADSIDE GAUGES (0.5, 2.5 and 4.5 m positions) | | | | | | |
| Mean (n = 22) | 5.6 | 94 | 452 | 1.56 | 3.9 | 0.30 |
| RSD (%) | 19 | 46 | 134 | 107 | 77 | 97 |
| Range | 3.9-6.7 | 21-181 | 12.4-1974 | 0.25-6.18 | 0.7-11.2 | 0.04-1.01 |
| FARM GAUGE | | | | | | |
| Mean (n = 4) | 4.9 | 71 | 22.9 | 0.04 | 1.7 | 0.02 |
| RSD (%) | 23 | 57 | 81 | 80 | 86 | 50 |
| Range | 3.7-6.1 | 15-105 | 1.2-46.3 | 0.01-0.08 | 0.4-3.1 | 0.01-0.03 |
| Significance levels of differences between means | <0.9 | <0.9 | >0.99 | >0.98 | 0.9-0.95 | >0.99 |

RSD = Relative Standard Deviation

For TS, TVS, COD, Zn and Cd no deposition analyses were undertaken, so appropriate literature values of background concentrations were sought. Those used for comparison with runoff data from the present work are given in Table 5.4 with relevant references. These values and those in Table 5.3 will be referred to in Sections 5.5.1-5.5.8 as required.

TABLE 5.4 : Literature values for background content of total deposition

| Parameter | Concentration | Reference |
|---|---|---|
| Total solids | 21.3 $mgl^{-1}$ | Harrop (1983) |
| Total volatile solids[a] | 46.6 $mgl^{-1}$ | Harrop (1983) |
| Chemical oxygen demand | 9-65 $mgl^{-1}$ | Harrop (1983) |
| Zinc | 85 $\mu gl^{-1}$ | Cawse and Pierson (1972) |
| Cadmium | <2 $\mu gl^{-1}$ | Cawse and Pierson (1972); Pope et al. (1979) |

[a] = sum of volatile dissolved and volatile suspended solids

## 5.5 Summary of Motorway Runoff Quality

### 5.5.1 pH and Electrical Conductivity

Data for these two parameters are summarised in Table 5.5, where mean values are also compared statistically with the farm data in Table 5.3. Of the 189 individual samples measured for pH, 117 arose from winter events and 72 from summer. The very low RSD (7%) of the 189 runoff values and the significantly lower mean and higher RSD from the farm data suggests that contact with the road surface exerts a marked buffering and neutralising action on pH variations in rain. A similar difference between rainfall and motorway runoff pH value has noted by both Pope et al. (1978a) and Bellinger et al. (1982). These authors found runoff pH ranges similar to those in the present work - 5.5 to 7.0 for three events (Pope et al., op. cit.) and event averages of 6.55 to 8.04 over eleven events (Bellinger et al., op. cit.). The tendency for runoff pH to increase by between 0.5 and 1.0 pH units during the course of an event as noted by Pope et al. (op. cit.) was not particularly evident during the present work.

TABLE 5.5 : pH and conductivity data

| | pH | Electrical Conductivity | | |
|---|---|---|---|---|
| | | Winter | Summer | All Year |
| RUNOFF | | | | |
| Mean | 6.3 | 3559 | 212 | 2212 |
| n | 189 | 211 | 142 | 353 |
| RSD (%) | 7 | 138 | 53 | 187 |
| Range | 5.4-7.6 | 54-22000 | 25-552 | 25-22000 |
| DEPOSITION AT FARM | | | | |
| Mean (n = 4) | 4.9 | - | 71 | - |
| RSD (%) | 23 | - | 57 | - |
| Range | 3.7-6.1 | - | 15-105 | - |
| Significance levels of differences between means | 0.9-0.95 | >0.99 (cf summer deposition) | >0.99 | >0.99 (cf summer deposition) |

The most notable feature of the conductivity data is the very large difference between winter and summer means, and demonstrates the enormous influence of de-icing salt application during winter on dissolved solids levels. The higher winter RSD and range values show that, in the absence of salting, conductivity levels can fall back to near-summer values, thus giving a very wide spread of winter values. Sixty-three percent of winter values were higher than the highest summer value (552 $\mu S\ cm^{-1}$) however. The difference between the winter runoff and farm deposition means is, as expected, statistically significant at a very high confidence level, but this is also true for the difference between the farm value and the summer runoff mean, indicating that even when effects of salting are discounted and background deposition (wet and dry) taken into account, the motorway surface itself contributes a significant dissolved solids load to runoff.

In-storm conductivity changes were very noticeable in most events, with a 50% reduction from initial levels within thirty minutes of the start of runoff being quite common (Fig. 5.9). As noted by other authors (Hedley and Lockley, 1975), dissolved solids therefore show a clear "first flush" tendency during the course of an event. In general, the range of values found over the entire sampling period during the present work is comparable with that reported in other highway runoff studies (Cathelain et al., 1981; FHWA, 1981a, Klein, 1982).

### 5.5.2 Total Solids and Total Volatile Solids

Total solids (TS) FWM data (from Appendix 6) is presented in Fig. 5.10, and the spread of values over two orders of magnitude is immediately apparent. The ten highest values all arose from winter events, and this was undoubtedly due to the very considerable influence of sodium chloride content in the samples, since these ten values correspond closely with events having high $Cl^-$ FWM values; the correlation coefficient between winter TS and $Cl^-$ FWMs was 0.998. The great influence of dissolved solids on the winter TS values is clear from the comparison with TSS FWM values for the same events which have been plotted on the same figure. The TSS winter values clearly cover a much smaller range (93-287 $mgl^{-1}$) than the TS data (96-10550 $mgl^{-1}$), and the difference between suspended and total solids concentrations

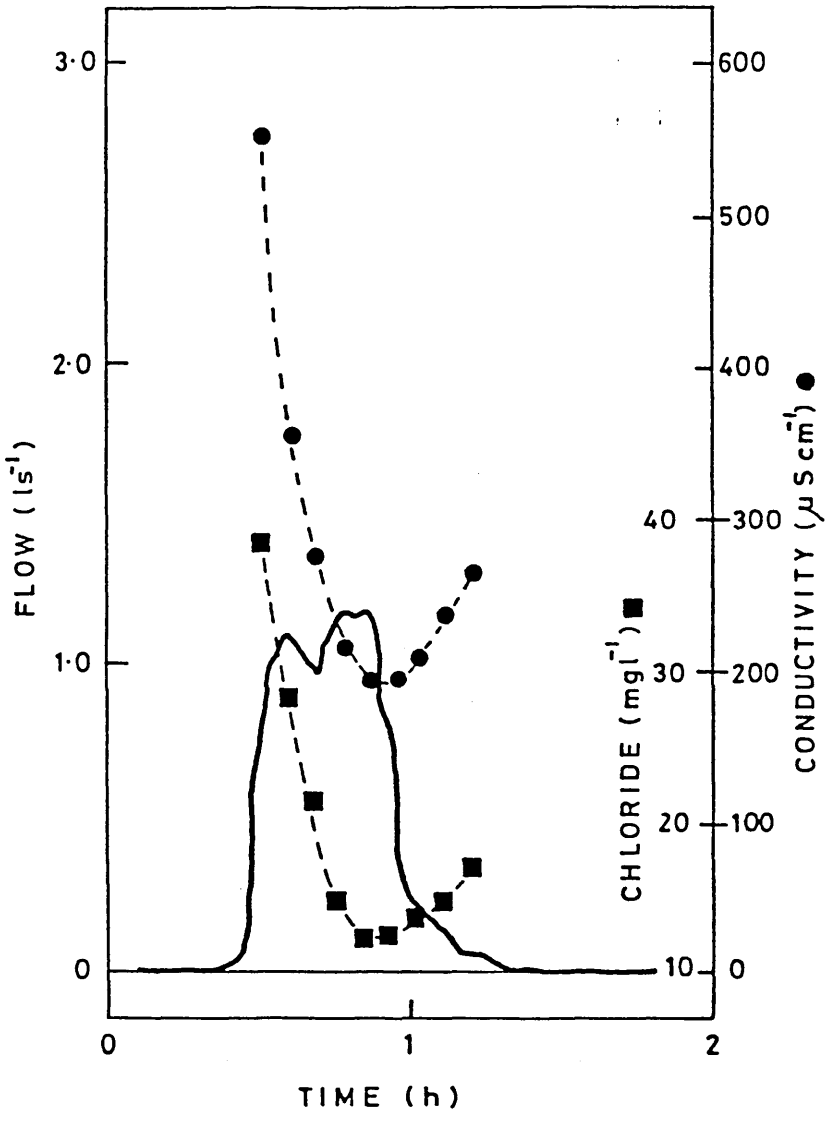



Figure 5.9 Typical hydrograph showing in-storm conductivity and chloride concentration changes

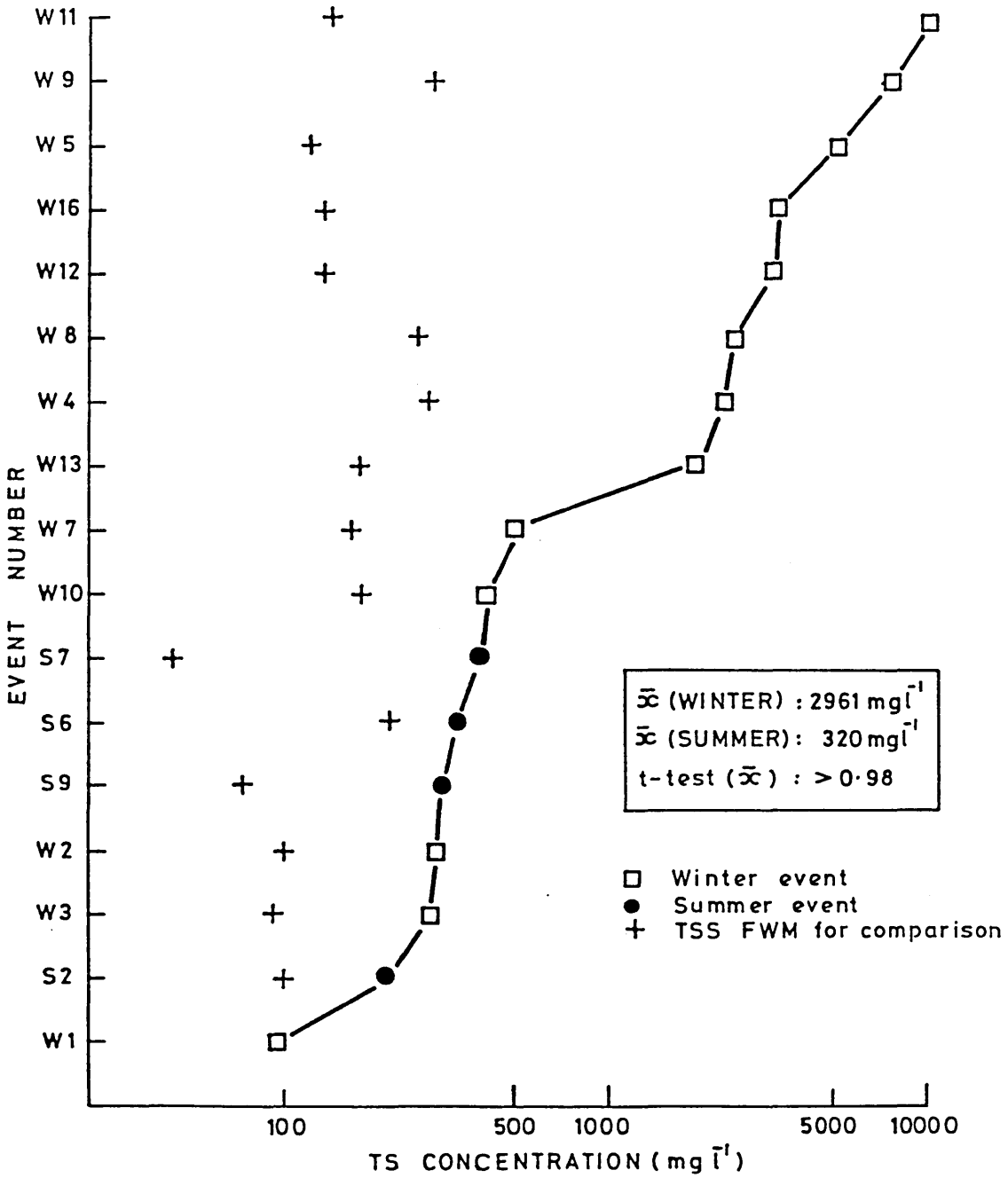



Figure 5.10 Total solids FWM concentrations

becomes larger and larger as the upper values of the TS data are reached. For many winter events, dissolved solids contribute more than 85% of the TS load.

The small number of summer data points in Fig. 5.10 compared with winter is due to a recurring problem with TS determinations in summer samples. Comparison of TS and TSS FWM values for summer events showed that TSS values were often significantly higher than TS values. This usually occurred for events where high runoff flow rates produced high TSS concentrations (Section 5.5.4(a)). The TS-TSS data discrepancy was attributed to frequent difficulty in producing an homogeneous distribution of suspended solids throughout an individual sample prior to subsampling for TS determination. Very rapid settling of heavier particles meant that subsamples frequently contained an unrepresentatively low TSS concentration, leading to the discrepancies observed. Thus TS data from summer events have only been included where TS and TSS concentrations show a reasonable relationship to one another, which occurs in four of the summer events analysed. The difference between seasonal means (Fig. 5.10) is statistically highly significant, but because of the problem with TS analyses the distribution of FWM values between winter and summer indicated in Fig. 5.10 may not be truly typical. Nonetheless, winter TS values are likely to dominate the upper range of the annual distribution of values because of salting effects.

The work of Söderlund and Lehtinen (1972) and the FHWA (1981a) are the only studies of those reviewed in Section 1.1 which reported TS data from long-term studies of highway catchments, but in both cases reported ranges are comparable to the present work. Söderlund and Lehtinen (op. cit.) reported a mean individual sample value of 855 $mgl^{-1}$ from 50 events and a maximum of 2800 $mgl^{-1}$. The FHWA report (1981a) gave an annual FWM mean of 1400 $mgl^{-1}$ and range of 145-21640 $mgl^{-1}$ for a site with a 100% paved area, compared with an annual FWM mean of 2340 $mgl^{-1}$ and range of 96-10550 $mgl^{-1}$ from the present work. Upper values from most studies will of course depend on the level of de-icing salt application during sampling.

The site from which this FHWA data was reported is the only one of the five studied which is strictly comparable to the M1 site, being

100% paved. References to data from this study will henceforth refer only to that site, unless otherwise stated.

Total volatile solids (TVS) FWM data is presented in Fig. 5.11. Since TVS determinations followed on directly from TS analyses, only TVS data from those summer events for which TS data were considered reliable have been included in Fig. 5.11. One summer value was less than the detection limit of the analytical method, so only the winter mean has been given.

Figure 1.1 (Section 1.1) illustrated the main sources of runoff contaminants on an urban road surface, but in a rural motorway catchment, such as the M1 site, the main sources of volatile organic material are likely to be carbonaceous material from soil and dust particles (wind blown or deposited by vehicles), wind blown plant debris, oil and grease (especially from total loss lubrication systems), bitumen, products of tyre wear and probably, to a lesser extent, vehicle emission products. The literature values for rainfall TVS (Table 5.4) suggest that the background deposition contribution at the M1 site could at times be significant.

As noted for TS data, the distribution of summer values may not be entirely representative of the true situation, but nonetheless the dominance of winter data in the upper range of both TS and TVS curves suggests that the presence of large concentrations of de-icing salt in runoff (reflected as high TS concentrations) may cause an increase in organic content.

This possibility was noted by Hedley and Lockley (1975), who observed a positive correlation between increases in winter suspended solids concentrations (attributed to de-icing salt solids) and increases in volatile SS concentrations. No completely satisfactory explanation was offered, but it was suggested that one possible source of increased volatiles was a scouring effect by rock salt particles on accumulations of greasy, oily dirt on vehicle undersides. Salt-induced damage to the bitumen surface of their study site was proposed as another possible explanation. The potential extent of this latter problem was the subject of a survey of UK highway authorities by Williamson (1968), who found that nine out of the thirty authorities surveyed suspected that de-icing salt had contributed to accelerated

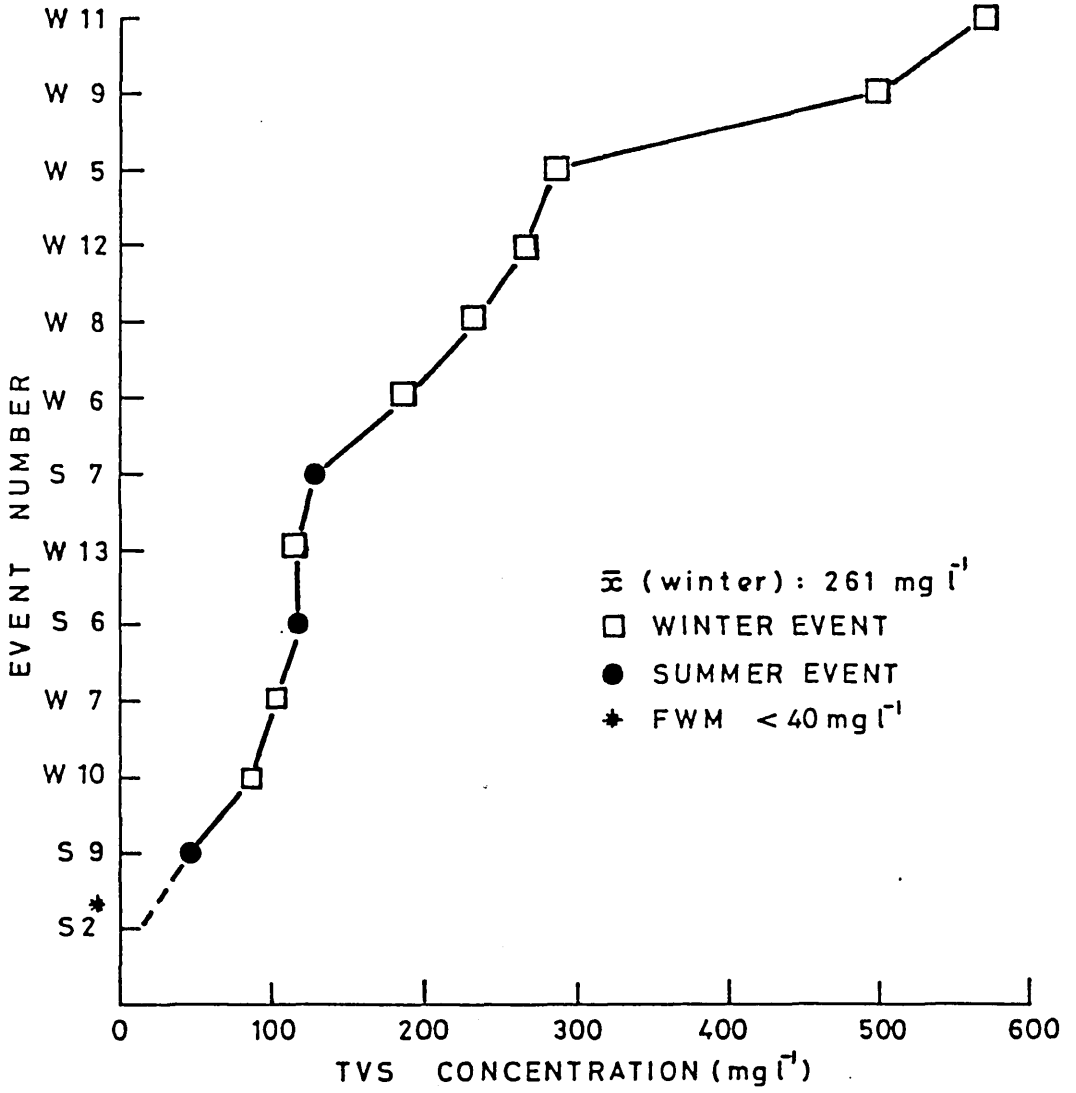



Figure 5.11 Total volatile solids FWM concentrations

breakdown of bitumen surfaces. The mechanism was considered to be a physical rather than chemical action, due to the increased frequency of freeze/thaw cycles after salt is applied. This effect has not, however, been particularly noticeable on the M1 in the site area (Butters, 1985). Trace organic impurities in de-icing salt may be another potential cause of higher winter TVS values. The FHWA report (1981a) did not monitor TVS data extensively, but the limited data presented indicated the possible existence of a similar seasonal trend for some of the sites monitored.

In general, therefore, the evidence available from this work and the sources quoted suggest that winter increases in highway runoff organic content may be fairly widespread, but the wider water quality aspects of this trend appear to have received little attention to date.

### 5.5.3 Chloride

#### (a) General Summary

The TS data in section 5.5.2 indicated clearly that de-icing salt would be expected to dominate winter $Cl^-$ concentrations, and, as expected, the $Cl^-$ FWM data presented in Fig. 5.12 shows that the uppermost values all arise from winter events. The t-test comparision demonstrates, as anticipated, a clear statistically significant difference between the seasonal means. While the highest summer FWM (S1) is 35.9 $mgl^{-1}$, the peak winter value is 156 times greater at 5590 $mgl^{-1}$. For two winter events (W1 and W3, Fig. 5.12), several events had occurred between these and previous salting applications, and consequently their FWM values (15.7 $mgl^{-1}$ and 24.8 $mgl^{-1}$) are comparable with those of summer events.

In individual events, the first flush phenomenon noted for EC (section 5.5.1, Fig. 5.9) was, as expected, observable with most events for which samples were analysed for $Cl^-$ individually, and the $Cl^-$ data in Fig. 5.9 illustrates this. In larger, more intense summer events, concentrations began to reach background levels (1-3 $mgl^{-1}$, Table 5.3) after rainfall of between 1.5-3 mm. Comparison of this background range with the range of summer FWM values (Fig. 5.12) indicates, however, that for most events background deposition does not

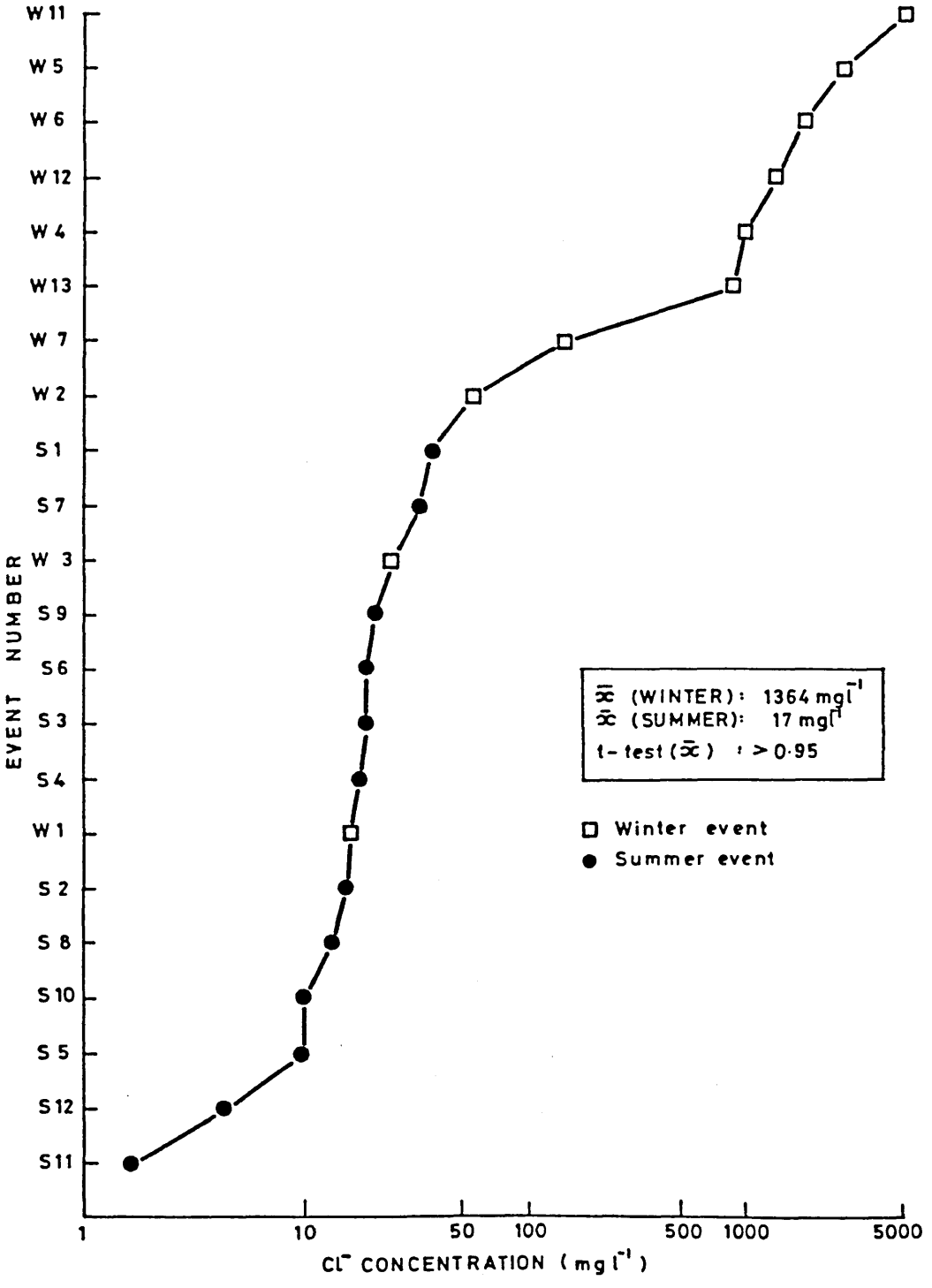



Figure 5.12 Chloride FWM concentrations

make a substantial contribution to $Cl^-$ concentrations. There was also some indication in summer events that the length of antecedent dry period affected the initial $Cl^-$ concentrations.

Literature values of highway runoff $Cl^-$ concentrations in the absence of salting are generally comparable with summer values from the present work. Dauber et al. (1978) reported a seasonal FWM of 22.4 $mgl^{-1}$ in runoff from the Swiss N1 motorway, Hedley and Lockley (1975) gave a monthly FWM range of 21-99 $mgl^{-1}$ for May-October 1976 (no salting), while the FHWA (1981a) reported a summer FWM range of 10-118 $mgl^{-1}$. Bellinger et al. (1982) in their M55 study, gave a range of 35-75 $mgl^{-1}$ for peak monthly concentrations (May-October 1976). Winter chloride values from other studies will of course be heavily influenced by the prevailing salting regime at the sites concerned during the time of sampling, so comparisons have a limited value. Winter ranges reported by the FHWA (1981a) and Hedley and Lockley are 62-13,380 $mgl^{-1}$ and 195-23,674 $mgl^{-1}$ respectively, while Bellinger et al. reported a peak value of 38,000 $mgl^{-1}$ from a January event, and Dauber et al. a peak value of greater than 1600 $mgl^{-1}$. The very wide range of values partly reflects the differences in total winter application rates reported, which ranged from 100 $gm^{-2}$ (Dauber et al.) to 2100 $gm^{-2}$ (Hedley and Lockley). The total for the present work was 560 $gm^{-2}$.

(b) Contaminants in De-icing Salt

Because $Cl^-$ concentrations in winter motorway runoff are often very high, samples of de-icing salt used on the M1 catchment were analysed for insoluble solids, Pb, Zn, Cd (and $Br^-$) as an initial stage in an assessment of the potential contribution of de-icing salt to the levels of these contaminants in runoff samples. The resultant data are presented in Table 5.6, and compare well with figures in Table 1.8 from Hedley and Lockley (1975) and the main suppliers of de-icing salt in the UK, ICI (1983). Salting contributions to TSS, Pb, Zn and Cd loads will be considered in Sections 5.5.4, 5, 6 and 7 following as appropriate, while $Br^-$ de-icing salt data is considered separately in section 6.

TABLE 5.6 : Results of de-icing salt analyses (4 samples)

| | | Mean Concentration ‡ | RSD (%) | Contribution from 1 g of chloride (mg) |
|---|---|---|---|---|
| Insoluble solids | (w%) | 6.23 | 14.8 | 115 |
| Chloride | (w%) | 54.0 | 2.4 | - |
| Bromide | (mg $kg^{-1}$) | 230 | 4.4 | 0.42 |
| Lead | (mg $kg^{-1}$) | 6.5 | 54.4 | 0.012 |
| Zinc | (mg $kg^{-1}$) | 15.5 | 17.4 | 0.029 |
| Cadmium | (mg $kg^{-1}$) | <2 | - | <0.004 |

‡ All data relates to undried sample i.e. as applied
RSD = Relative Standard Deviation

5.5.4 Total Suspended Solids

(a) General Summary

Figure 5.13 presents TSS FWM data. The highest value (2310 $mgl^{-1}$) is more than three times higher than the next lowest (723 $mgl^{-1}$), and arises largely from a single sample within a short event (S8) which had an exceptionally high TSS concentration (3431 $mgl^{-1}$). This uppermost value was thus excluded from the t-test comparison of mean FWM values (Fig. 5.13), on the grounds that its inclusion would lead to excessive distortion of the trends evident in the remaining data. For this reason also, the concentration scale in Fig. 5.13 has been shown in linear rather than log form in order to bring out the trends in the remaining data more clearly.

A notable feature of Fig. 5.13 is that the six uppermost FWM values arise from summer events, although the seasonal means are not significantly different at $P \geq 0.9$. In many events sampled (winter and summer), increases in runoff flow rates were very often observed to lead to increases in TSS concentrations, and Fig. 5.14 gives an example of this. This effect is almost certainly due to increased scouring of the road surface and mobilisation of heavier solids at

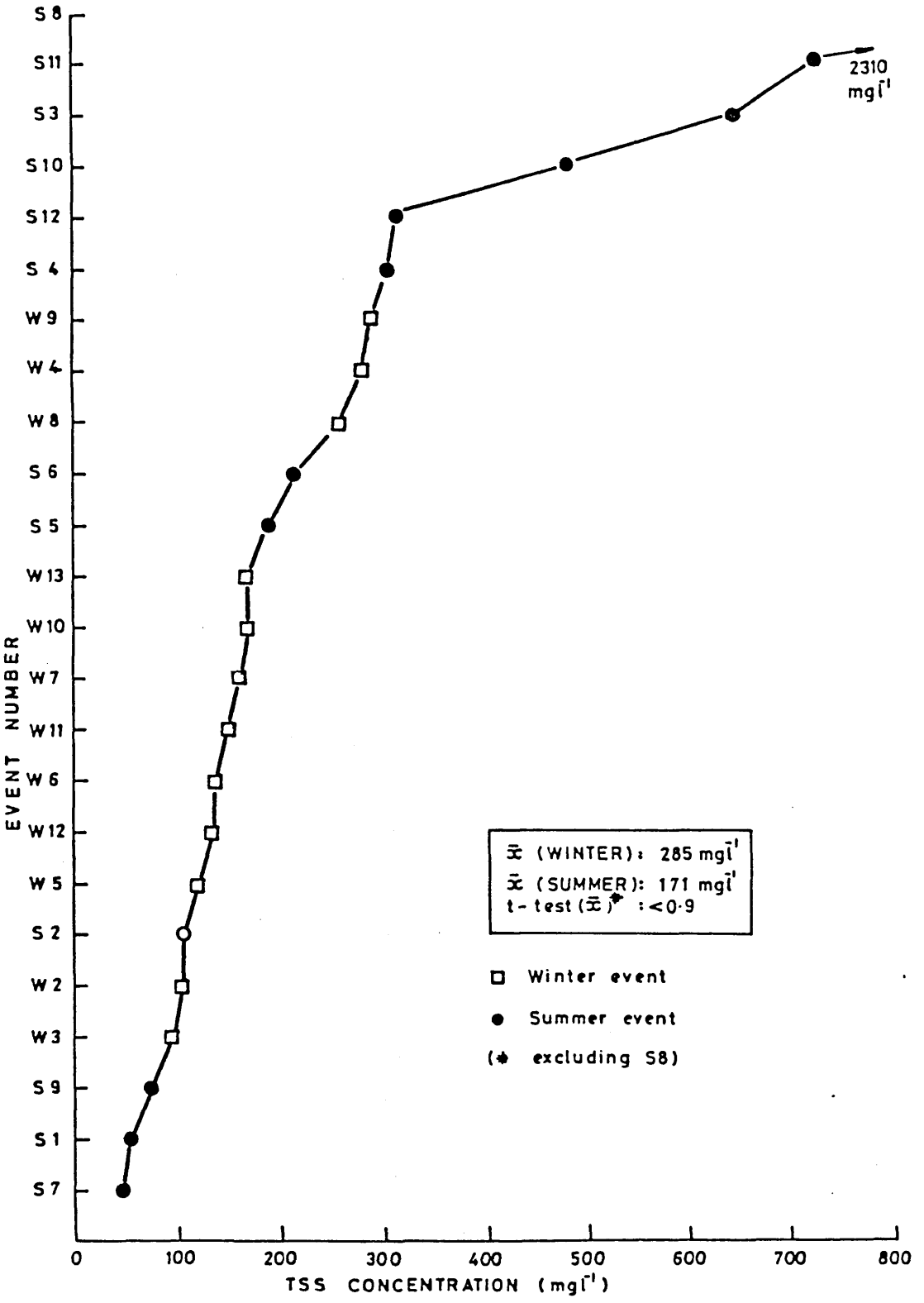



Figure 5.13 Total suspended solids FWM concentrations

higher flow rates. Event mean flow data in Table 5.2 showed clearly that mean flows tend to be significantly higher and cover a wider range in summer than in winter, so it is very probable that the trend to higher TSS FWM values in summer (Fig. 5.13) is due principally to this effect. Nonetheless, the magnitude of this was variable, and a first flush of TSS was not often observed if flow rates during the early part of an event were less than 0.2-0.3 $ls^{-1}$, as evident in Fig. 5.14.

The lack of a statistically detectable difference between TSS seasonal means may be partially due to the wider range of mean flows in summer, which in turn leads to the wider range of FWM values observed in summer (51.3 to 723 $mgl^{-1}$ cf 93.2-287 $mgl^{-1}$ in winter). This leads to a wider spread of data around the summer FWM mean (Fig. 5.13) and a correspondingly smaller likelihood of detecting a significant seasonal difference.

(b) De-icing Salt Solids

Apart from the wider range of TSS FWM values in summer, another factor which may be of equal importance in affecting seasonal differences is a potential contribution to TSS loads from the residual solids in de-icing salt. Both Hedley and Lockley (1975) and Bellinger *et al.* (1982) noted a peak in suspended solids concentrations during periods of de-icing activity. An attempt has therefore been made in the present work to estimate the possible salting contribution to the winter TSS loads recorded.

The following procedure was adopted. Using the winter $Cl^-$ load data in Appendix 5 and the data for de-icing salt solids content in Table 5.6, the amount of salt-derived solids presumed to be originally associated with the $Cl^-$ load of each winter event was calculated. A small correction to winter $Cl^-$ loads for a "non-salt" element was first made by subtracting an appropriate figure derived from the product of the summer $Cl^-$ FWM mean (16.7 $mgl^{-1}$) and the sampled volume for each winter event. Estimated salt-derived TSS loads were then summed for all winter events analysed for $Cl^-$, and the result compared with the sum of recorded TSS loads for the same events. This approach was adopted in order to minimise as far as possible the effects of different degrees of $Cl^-$ and TSS removal in individual events, due to the

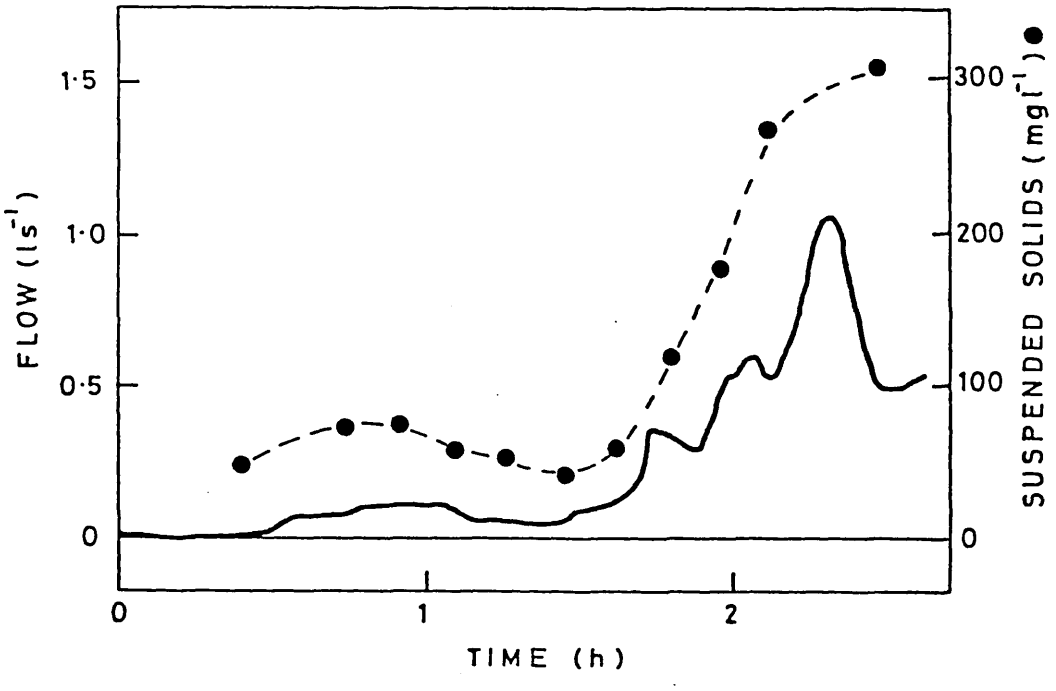



Figure 5.14 Typical hydrograph showing in-storm changes in TSS concentrations

different removal patterns noted in 5.5.3(a) and 5.5.4(a) respectively.

This procedure led to a figure for the total salt-derived solids load of 1730 g, or 55% of the total recorded TSS load of 3170 g for the nine events analysed for $Cl^-$. Although this figure can only be regarded as indicative, it strongly suggests that de-icing salt can contribute significantly to winter TSS loads. In the light of the trend to higher summer TSS concentrations noted above, however, it appears that other factors may be operating to reduce the apparent impact of salting solids on differences in seasonal means. These factors may include:

(i) The low percentage (~20%) of fine, easily mobilised solids in the salt solid content.

(ii) The removal of salt-derived solids from the carriageway by mechanisms other than runoff, especially by wind action (deflation).

(iii) The possibility of salt-derived TSS loads being imposed upon salt-free winter load levels which are significantly lower than that suggested by Fig. 5.13.

Examination of the solids obtained by dissolving and filtering samples of de-icing salt revealed that in the region of 20% consisted of fine clay-like material which would be easily mobilised by the low flows characteristic of winter events. The remaining 80% generally consisted of grit-like particles (1-3 mm diam) which would be much less likely to be removed by runoff, and this would therefore reduce the potential impact of salting solids on TSS loads.

This factor may also have acted in conjunction with (ii) above to reduce residual salt solids loadings. Evidence that removal by wind action (arising from either prevailing winds or vehicle-induced turbulence) arose from TSS deposition data, from which it was clear that solids deposition was much greater at 0.5 m from the carriageway than at 4.5 m, although rainfall did not vary much between these positions. The data are summarised graphically in Fig. 5.15, with relevant mean values and statistical data. Values for dry deposition are included for comparison.

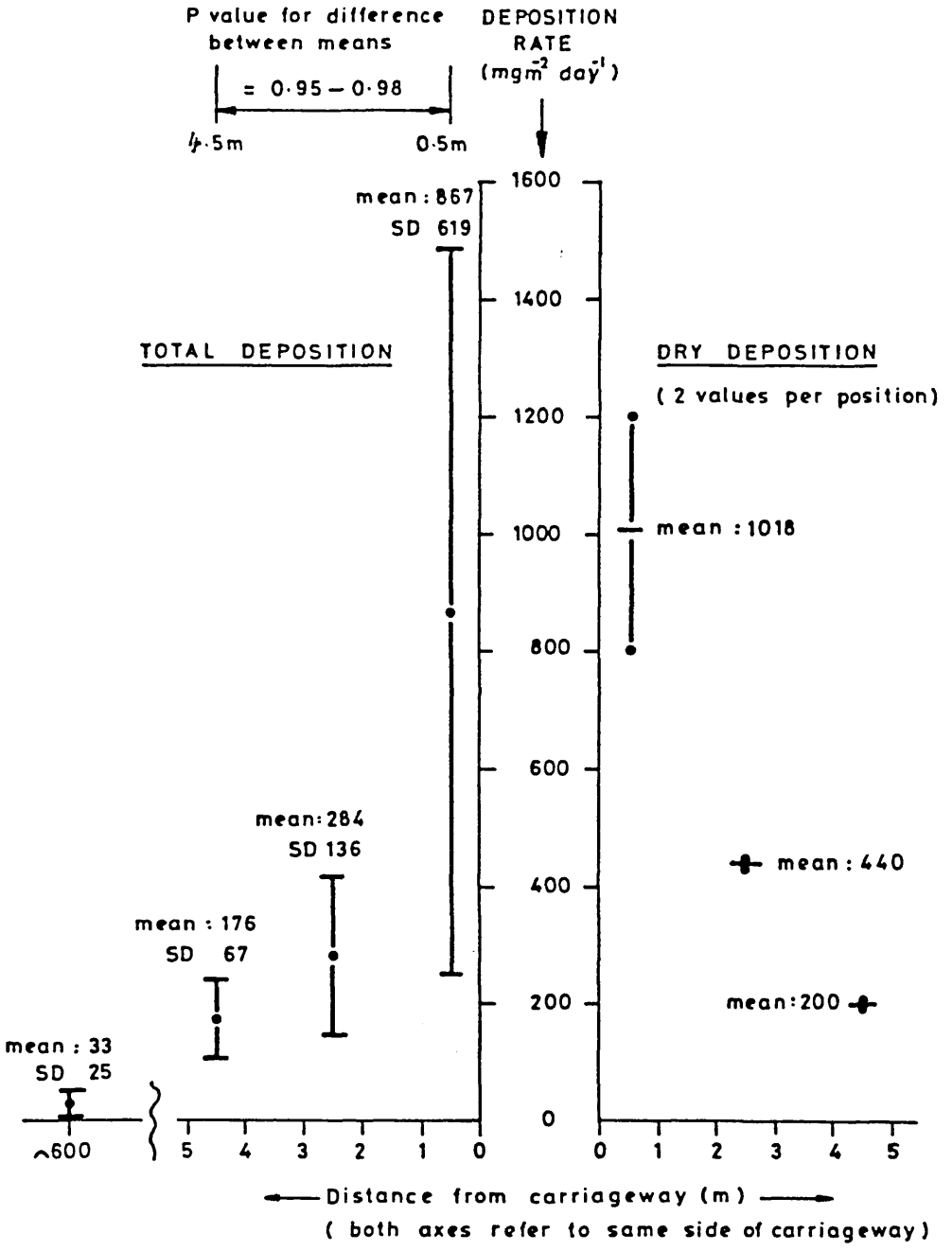



Figure 5.15 Total suspended solids deposition rates

The data presented show clearly that the great majority of solids deposited within 5 m of the carriageway arose from the motorway itself. The dry deposition data, although limited, clearly indicates that this process takes place independently of rainfall, and is probably continuous in the presence of normal vehicle flows. Although the data were derived from summer sampling, it is clear that any residual salt-derived solids remaining on the carriageway after a runoff event could well be removed in this way. From the author's personal observation, vehicle-induced turbulence can cause very disturbed air movement at the road surface, sufficient to move large particles of grit and maintain a continuous scouring action.

Concerning factor (iii) above, it was not possible to draw any firm conclusions concerning the general level of winter TSS concentrations in the absence of salting from the data available. Only two winter events (W1 and W3) show $Cl^-$ FWM values within the summer range (15.7 and 24.8 $mgl^{-1}$ respectively), but TSS data for W1 are not available and the FWM value for W3, 93.2 $mgl^{-1}$, is also within the summer range.

Studies by other workers which report the effects of de-icing salt on TSS loadings in highway runoff are those of the FHWA (1981a) Asplund *et al.* (1982), Hedley and Lockley (1975) and Bellinger *et al.* (1982). Comparisons with the first two (American) studies, however, are rendered invalid owing to the practice of adding sand to de-icing salt in the USA. The studies of Hedley and Lockley and Bellinger *et al.* therefore provide more relevant comparisons.

The former reported a range of monthly TSS FWM values of 547-2599 $mgl^{-1}$ over the period of salt application (November 1973 - March 1974) compared with a summer range of 134-1204 $mgl^{-1}$, while Bellinger *et al.* reported TSS FWM values for a total of 11 storms, three of which were influenced by salting. For these three, the TSS FWM range was 55.5-404.9 $mgl^{-1}$, while for the remainder, both winter and summer, the range was 11.8-58.5 $mgl^{-1}$. Both authors concluded that the increases in winter TSS concentrations observed were due to the effects of de-icing salt, and, in the case of Hedley and Lockley's study, typical de-icing salt analyses showed that the solids content was similar to the present work.

These results were generally in contrast to those of the present work, but comparisons must take into account the markedly higher levels of total winter salt application recorded for these two studies - 2100 $gm^{-2}$ (Hedley and Lockley) and 915 $gm^{-2}$ (Bellinger et al.), as compared with 560 $gm^{-2}$ for the present work. It is also clear, in the case of Bellinger's study, that TSS FWM values in the absence of salting are generally much lower than in the present work, possibly because the carriageway studied was relatively new. This could serve to emphasize a salting TSS contribution. Hedley and Lockley's study area ran for two thirds of its length in a cutting, which would significantly reduce dispersion of solids from the carriageway by deflation. In neither study was any detail given of the prevailing gradients in the study catchments, which would be of great importance in determining runoff flow-rates and thus solids removal.

In general, therefore, it is clear that although the effects of salting on winter TSS levels are more marked in these two studies than in this work, a variety of detailed local factors must be taken into account when making comparisons, and it appears possible that much of the difference between the studies could be accounted for in the light of these.

Apart from de-icing salt, other possible sources of TSS loads in runoff include background deposition, vehicular particulate emissions, road surface degradation products, products of tyre, brake and clutch wear and dirt washed off the undersides of vehicles during runoff itself (Section 1.1.2). The farm site TSS concentration data (Table 5.3) and deposition rate figures (Fig. 5.15) compared with the respective roadside data indicate clearly that background deposition is not generally a significant contributor to TSS levels in runoff and that the great majority of TSS arises from the motorway itself. Most of the remaining sources, such as road surface degradation, are very difficult to quantity individually, and this has not been attempted in the present work except for tyre wear, for which estimates have been made as a stage in quantifying this as a source of Zn and Cd (Sections 5.5.6 and 5.5.7). A more detailed statistical analysis of the general factors (e.g. runoff volume) which appear to govern TSS loads is given in Section 5.6.

(c) Nature of Suspended Solids and Particle Size Distribution

The TSS data discussed so far were all derived from analysis of individual 500 ml or composite 1000 ml samples. Since these samples provided insufficient bulk of solids for assessment of their composition and particle size distribution, the bulk suspended solids sampling programme (Section 2.4.1(b)) was undertaken to provide more information in these areas. A total of 12 sampling runs were completed, and data arising from these are given in Appendix 7. Particle size distributions as found on the sieves are summarised from that Appendix for 10 runs in Figures 5.16A and 5.16B. (Data has been spread over two figures to avoid excessive overlap of the curves). The "reference point" for the cumulative percentage data has been taken as the sum of the weights of solids found on the six mesh sizes, since it was not possible to measure the percentage passing the 100 μm mesh. In several of the sampling runs, blockages occurred with some of the smaller mesh sizes; the data points affected have been marked appropriately in the figures.

It is clear from the two figures that, in general, the distribution of particle sizes is very approximately log normal, and does not appear to have been seriously affected by the blockage problem. Apart from a limited amount of data reported by Pope et al. (1978a,b) which showed a similar trend to the present work, none of the highway runoff studies previously referred to in section 1.1 have included direct sieving of runoff solids, so comparisons with other data are limited. Ellis and Harrop (1983), however, report data from direct sieving of residential street runoff, which shows a generally log normal particle size distribution similar to the present work.

Sufficient quantities of solids were collected during sampling to permit a qualitative visual assessment of their composition on each sieve size, and a summary of characteristics is given in Table 5.7. The table makes it clear that the material found on the 1600 μm sieve is better classified as "litter" rather than as sediment, and a similar distinction was made by Ellis and Harrop (1983), who identified coarse road chippings and plant debris as some of the major components of the litter fraction. On two occasions, the 1600 μm sieve contained clearly indentifiable coal debris, indicative of a possible load

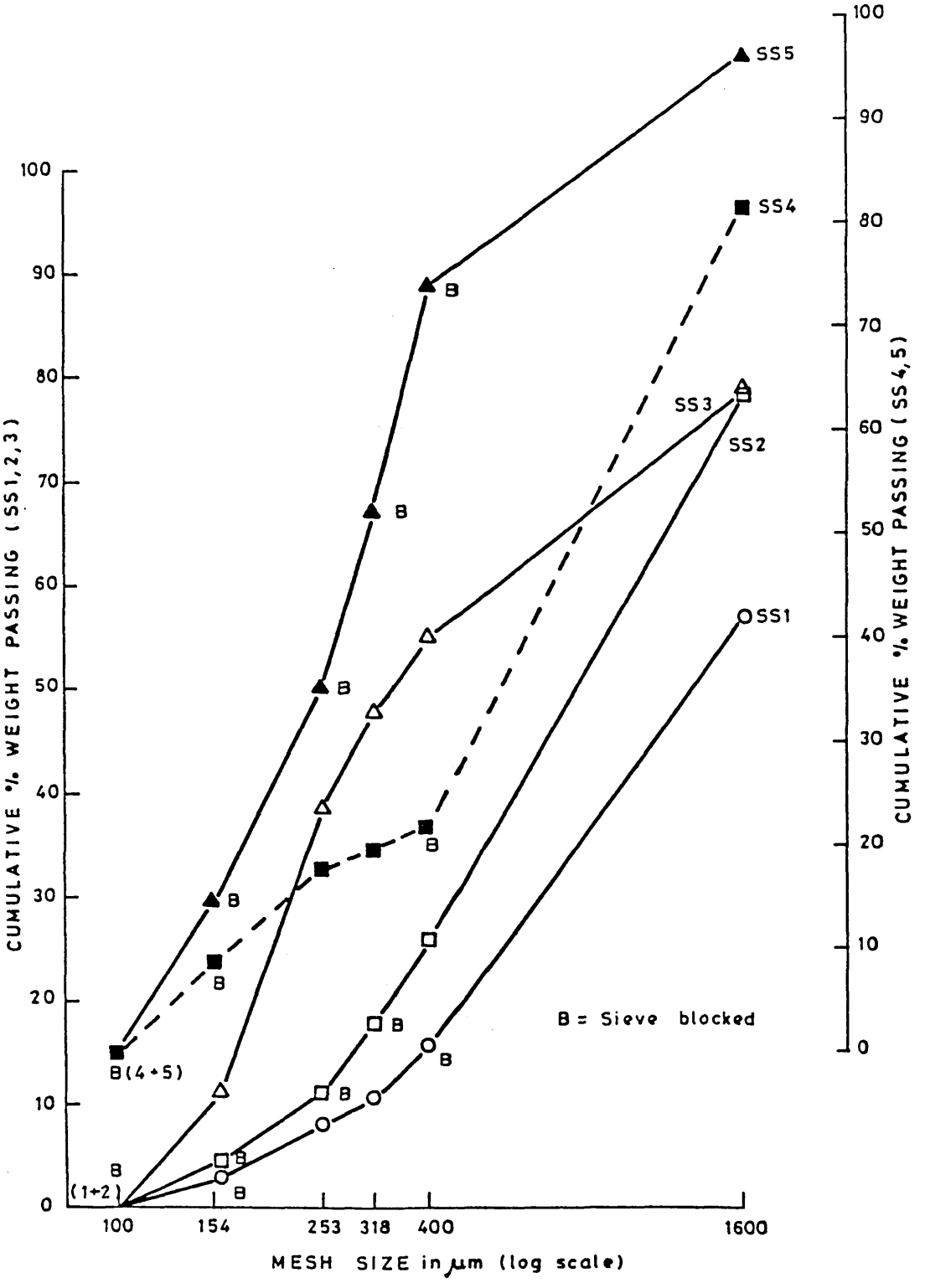



Figure 5.16A Sieve solids particle size data (runs SS1, 2, 3, 4 and 5)

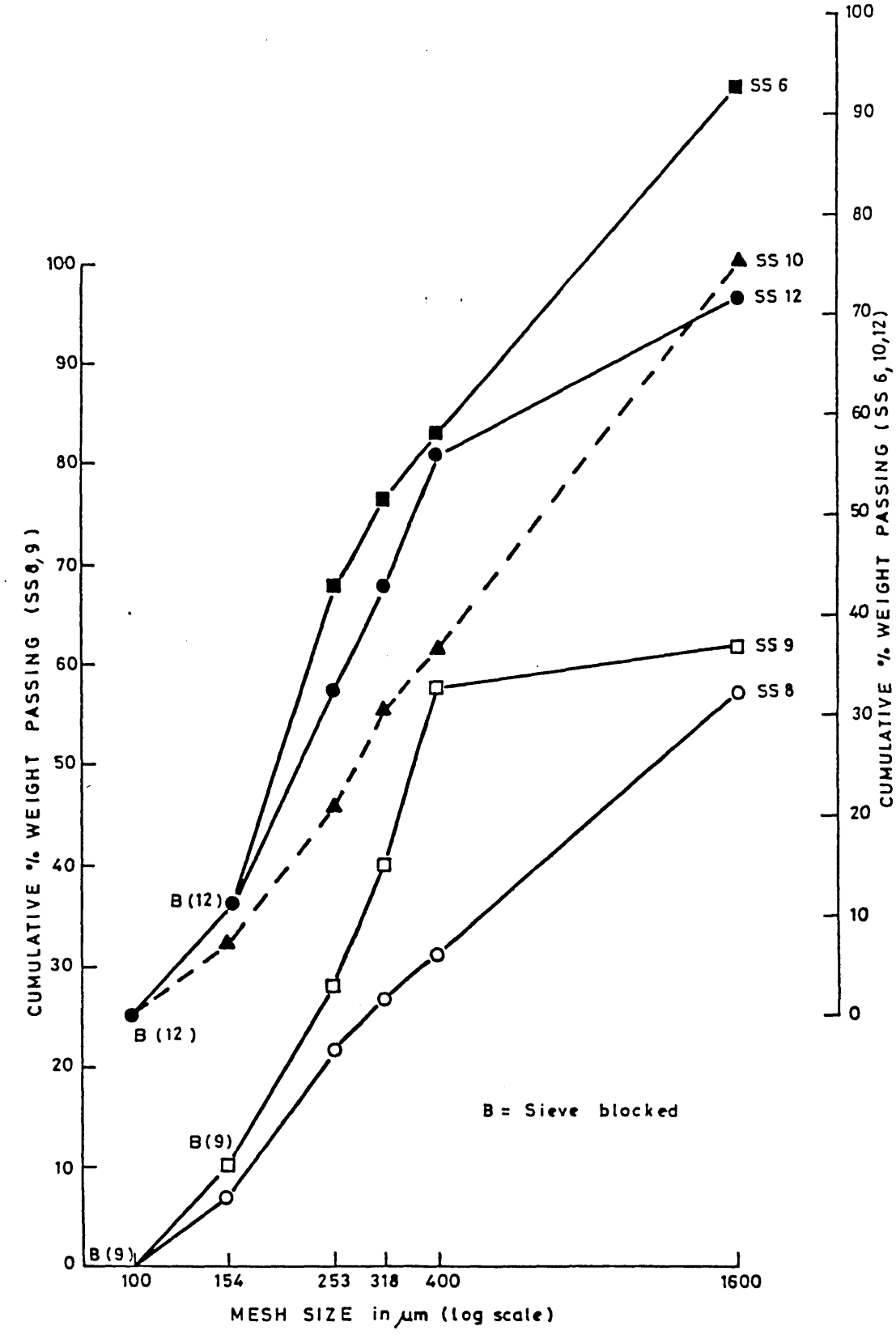



Figure 5.16B Sieve solids particle size data (runs SS6, 8, 9, 10, 12)

spillage during the sampling period. The frequent presence of small particles of brick in the 400 μm sieve was presumed to arise from the large number of lorries using the motorway to convey bricks southward from the large brickworks north of Bedford. There are no brick buildings or walls in the vicinity of the site which could have contributed the quantities found in the sieves.

TABLE 5.7 : Description of sieve solids

| Sieve Mesh Size (μm) | Description of Solids |
|---|---|
| 1600 | Chippings, plant debris, litter, cigarette ends, small flakes and shreds of rubbery, oily material, dead insects. Occasionally small fragments of brick and coal. |
| 400 | Mixture of matted, fibrous material and gritty, oily material interspersed with sticky lumps of oil/rubber mixture. Generally much denser and finer than 1600 μm material. Brown to black in colour when dry. |
| 318 | Gritty, matted, fibrous material, generally brown when dry. |
| 253 | Very similar to 318 μm |
| 154 | Very fine gritty, matted material |
| 100 | As 154 μm, except material now extremely fine. |

Table 5.7 indicates that, in general, the material on the sieves was heterogeneous in nature, and the term "particle" could only be loosely applied to it. It was clear that in many instances the "particles" found were agglomerations of originally finer material (e.g. tyre dust, road surface abrasion products) formed by contact with an oil/water mixture during runoff. In order to attempt an assessment of the effect of the wetting/agglomeration process on particle size, therefore, a further sieving exercise was carried out on samples from runs SS2, SS4 and SS6 following oil removal using the Soxhlet procedure, as described in Section 3.8.2(d). The data obtained from this experiment are presented in Fig. 5.17 (SS2), 5.18 (SS4) and 5.19 (SS6).

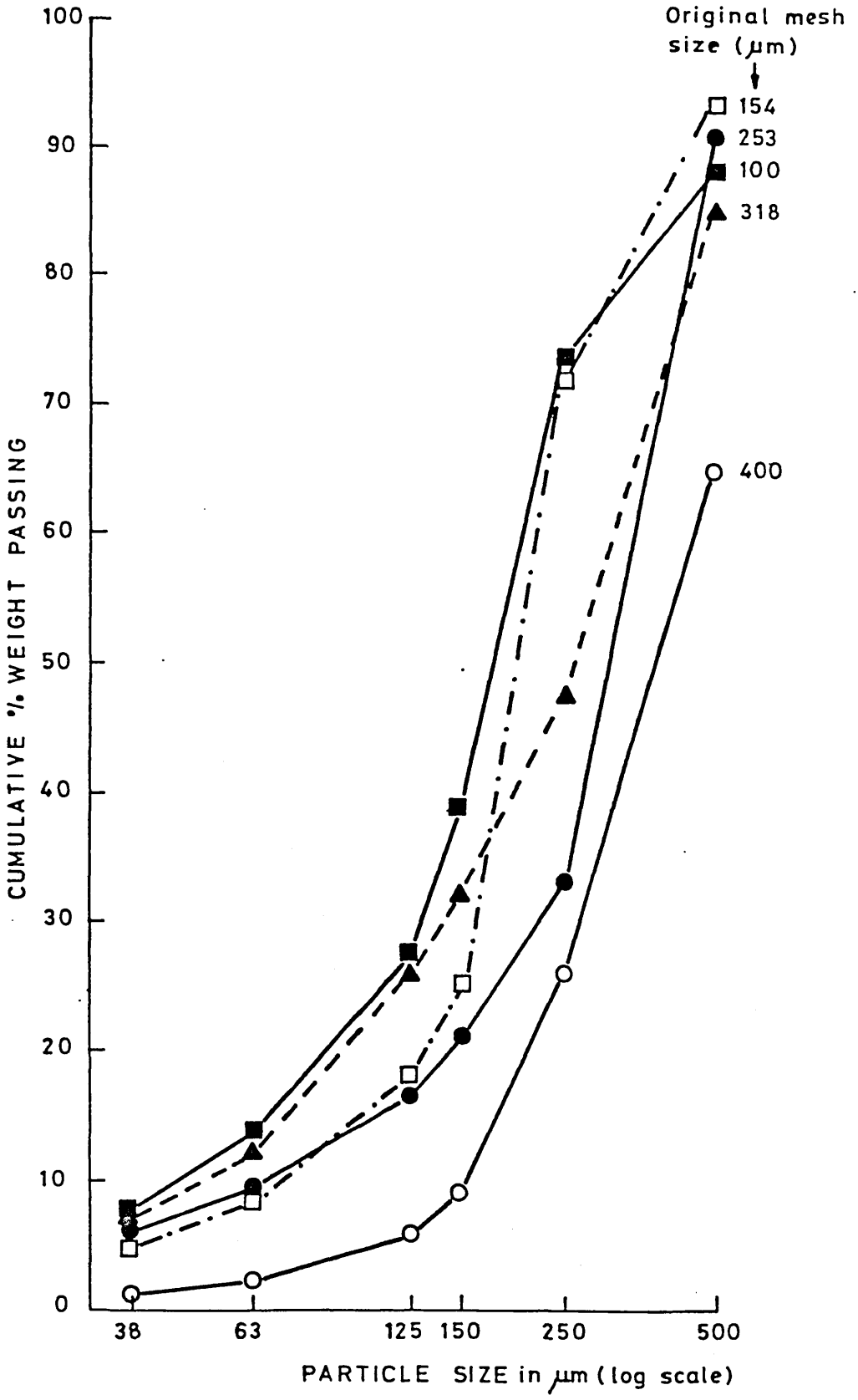



Figure 5.17 Particle size analysis of oil-free sieve solids (run SS2)

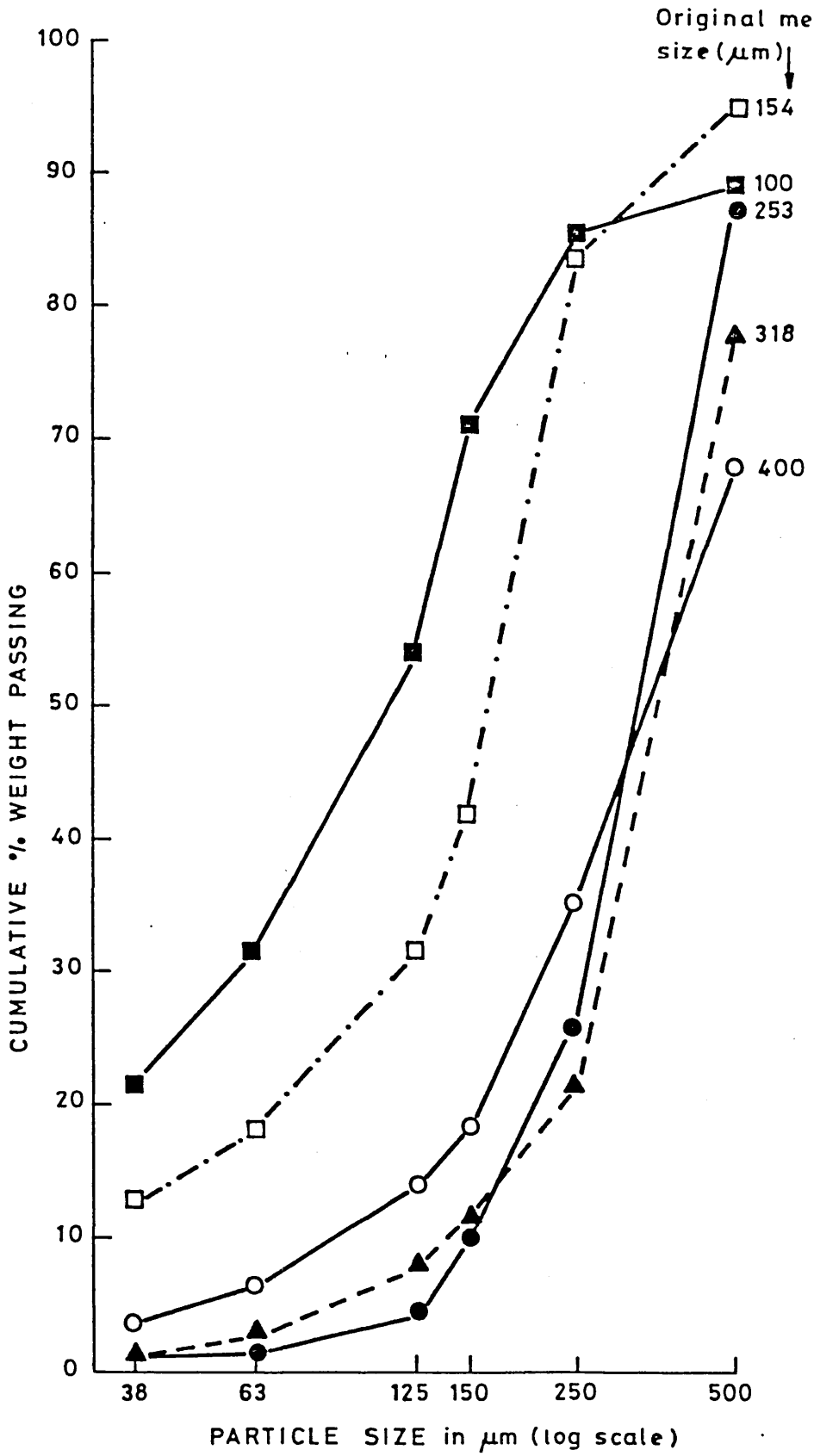



Figure 5.18 Particle size analysis of oil-free sieve solids (run SS4)

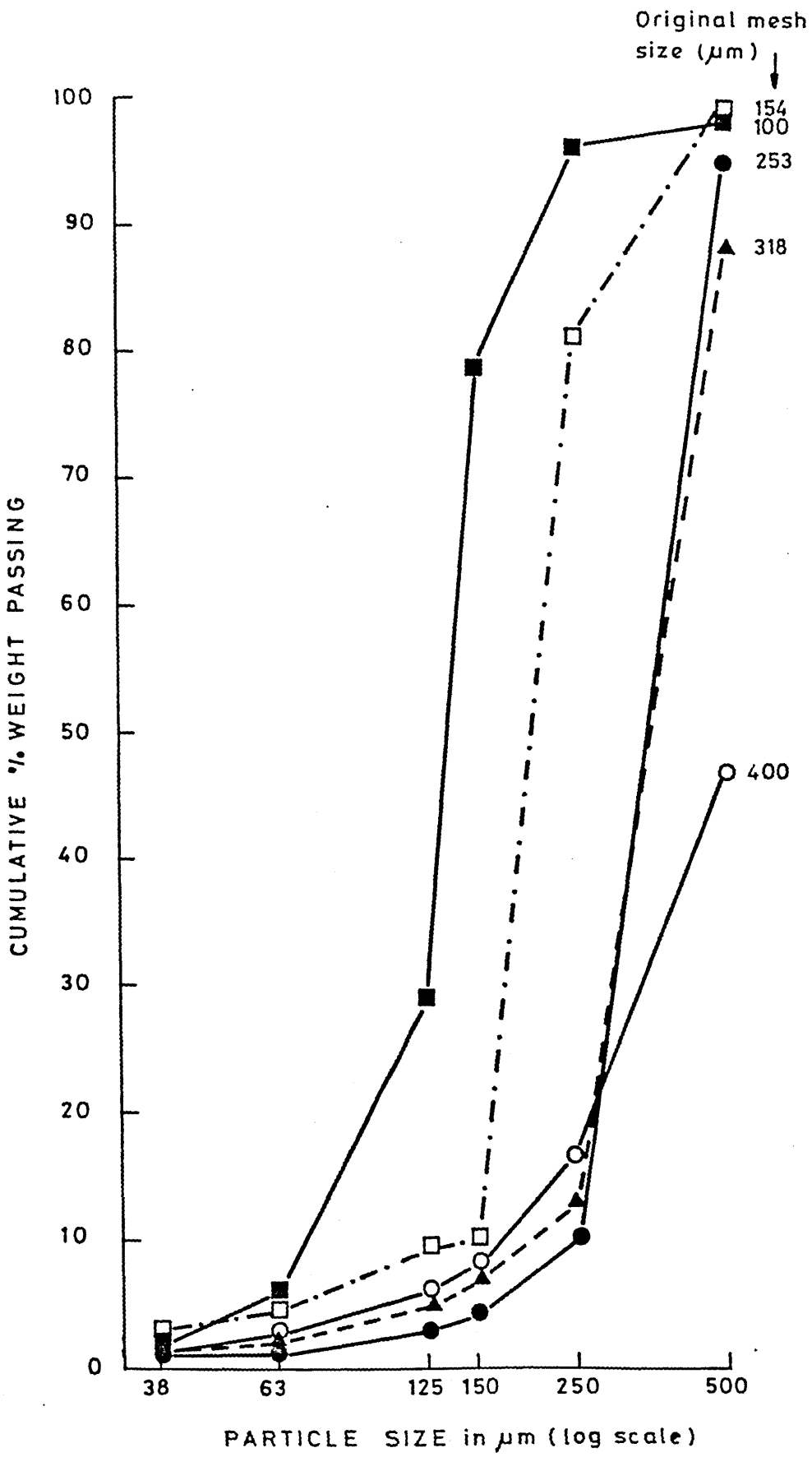



Figure 5.19 Particle size analysis of oil-free sieve solids (run SS6)

Comparison of these figures with Figures 5.16A and 5.16B for the wet sieved data indicates a clear tendency for the dry, oil-free solids to adopt a more definite log normal distribution, with a median particle size range for all three sets of curves of 120-370 μm. The data arising from a similar particle size analysis of two road dust samples are presented for comparison in Fig. 5.20, and the general shape of the curves is clearly similar to Figures 5.17-19, which tends to confirm that the effect of interaction of the dust with runoff is to alter the effective distribution of particle sizes.

From the data for the smaller sieve sizes in Figures 5.17-19 (i.e. 253 μm and less) it can be seen that on several occasions particles were found which were larger than the original preceding mesh size during sampling. This appeared to be due to the effects of drying on the extraction residues, which caused some of the fibrous material to form matted solids which were not always broken up by the sieving action. The effect was more marked when considerable amounts of fibrous material were present, as occurred in run SS2. This emphasises that the nature of runoff suspended solids and the effects of oil agglomeration must be taken into account when interpreting particle size data from direct (wet) sieving of road runoff.

### 5.5.5 Lead

#### (a) General Summary

The distribution of FWM values during the sampling period is shown in Fig. 5.21. The data exhibited a very similar pattern to the TSS data (Fig. 5.13) and the uppermost value (4350 $\mu gl^{-1}$) corresponds to the event (S8) giving rise to the highest TSS FWM. As in the case of TSS, this extreme value was largely due to a single sample with a very high Pb concentration (8015 $\mu gl^{-1}$), and has thus also been omitted from the t-test comparison of mean seasonal FWM values on similar grounds as those for its exclusion from the TSS seasonal comparisons.

The range of concentrations in Fig. 5.21 (200-4350 $\mu gl^{-1}$) is comparable to ranges reported by Cathelain *et al.* (1981), Klein (1982) and the FHWA (1981a), as well as those quoted by Harrop (1983) and Harrison and Wilson (1985a). Except for the FHWA work, the majority of reported values lie between 5 and 5000 $\mu gl^{-1}$, with the FHWA giving an extreme upper value of 13100 $\mu gl^{-1}$.

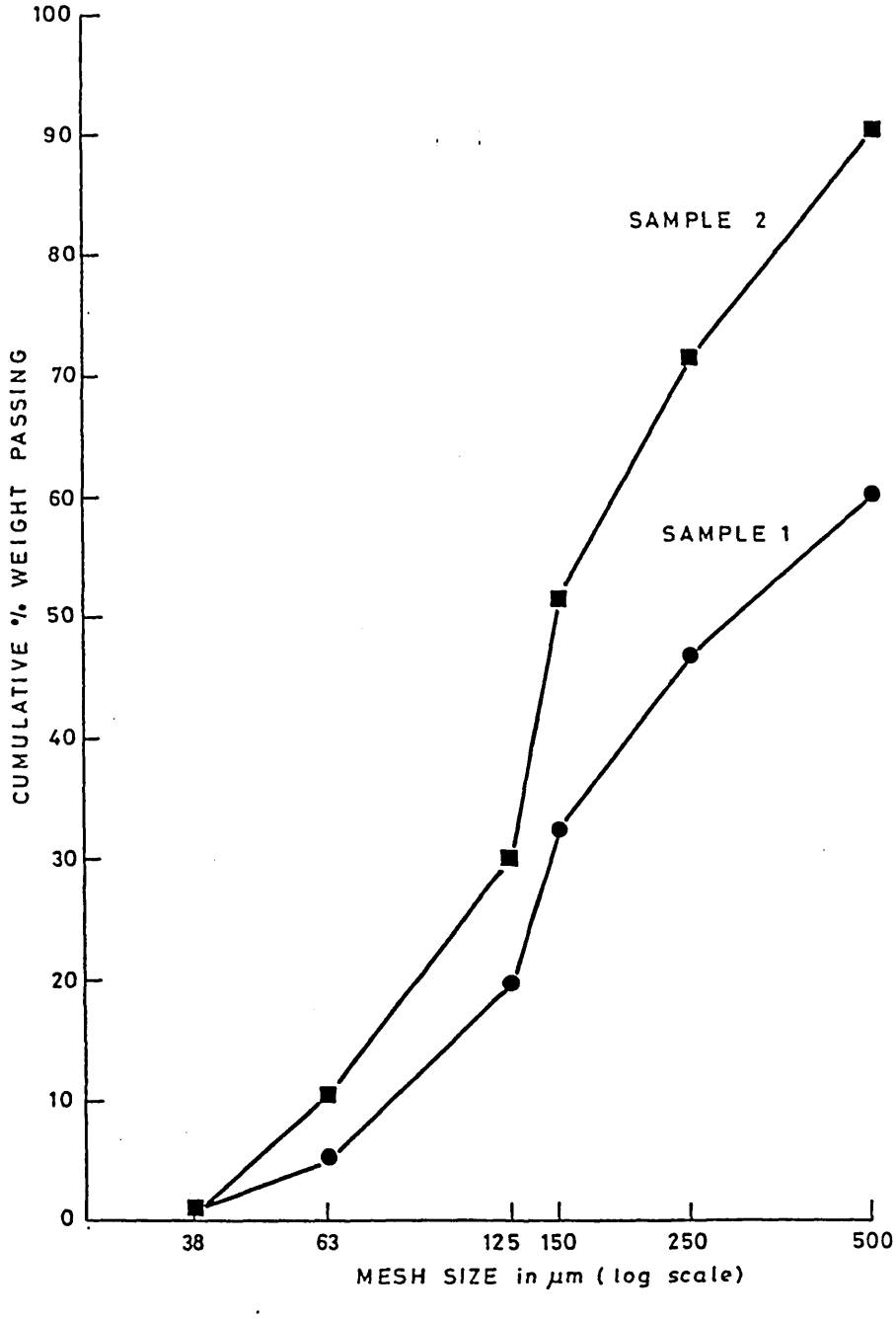



Figure 5.20 Particle size analysis of road dust samples

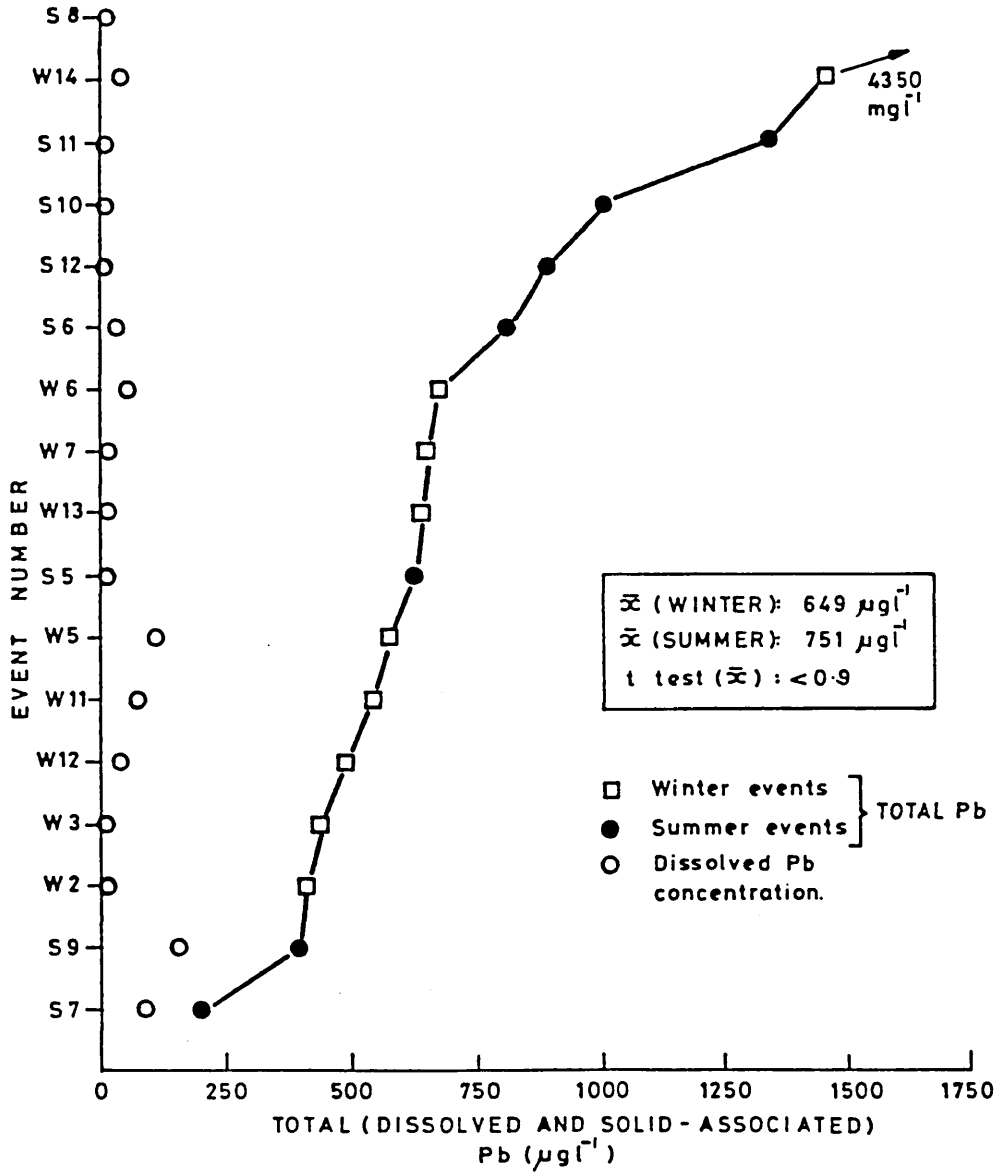



Figure 5.21 Total Pb FWM concentrations

The correlation coefficient between TSS and Pb FWM values was 0.811, and reflects the close association between Pb and suspended solids during the events which is evident in Fig. 5.22. This effect has also been noted in other studies (e.g. FHWA, 1981a; Harrison and Wilson, 1985a). This is also reflected in the similarity between the TSS and Pb FWM curves previously noted, so the lack of a statistically detectable difference between Pb seasonal means is not surprising, nor is the concentration of Pb summer event data in the upper part of the curve in Fig. 5.21, both trends reflecting similar tendencies in the TSS data.

In the samples themselves (single and composite) the majority of Pb content was also found to be solid associated. It was considered possible, however, that this may have been an effect partly due to sample storage prior to analysis, which was in most cases an unavoidable necessity due to the intervals between site visits and the sporadic nature of sampling runs. In addition, some adsorption of dissolved Pb by the filtration apparatus used for TSS determinations (section 3.2.4) was considered possible (Gardner, 1982). An investigation into these topics by Ofori (1984a) did not, however, find the effects of storage or filtration to be significant, so it was assumed that the degree of solid association in the samples generally reflects conditions in runoff itself.

The predominance of solid-associated Pb in runoff can be clearly seen in Fig. 5.21, where dissolved Pb FWM values for each event have been plotted separately for comparison with the points for total Pb (dissolved plus solid associated). Dissolved Pb concentrations in winter samples with high $Cl^-$ concentrations required correction for this by factors in the region of 1.5 (section 3.2.6(d)), but even after this the mean percentage dissolved component for all events was only 8.9% (SD 13.2%). In general, therefore, Pb movement during runoff would appear to be predominantly governed by those factors which affect TSS movement most, such as runoff volume and flow rates. As with TSS, the length of antecedent dry period did not appear to influence Pb levels to a great extent. A more detailed examination of factors affecting Pb loads is presented in Section 5.6.3(b).

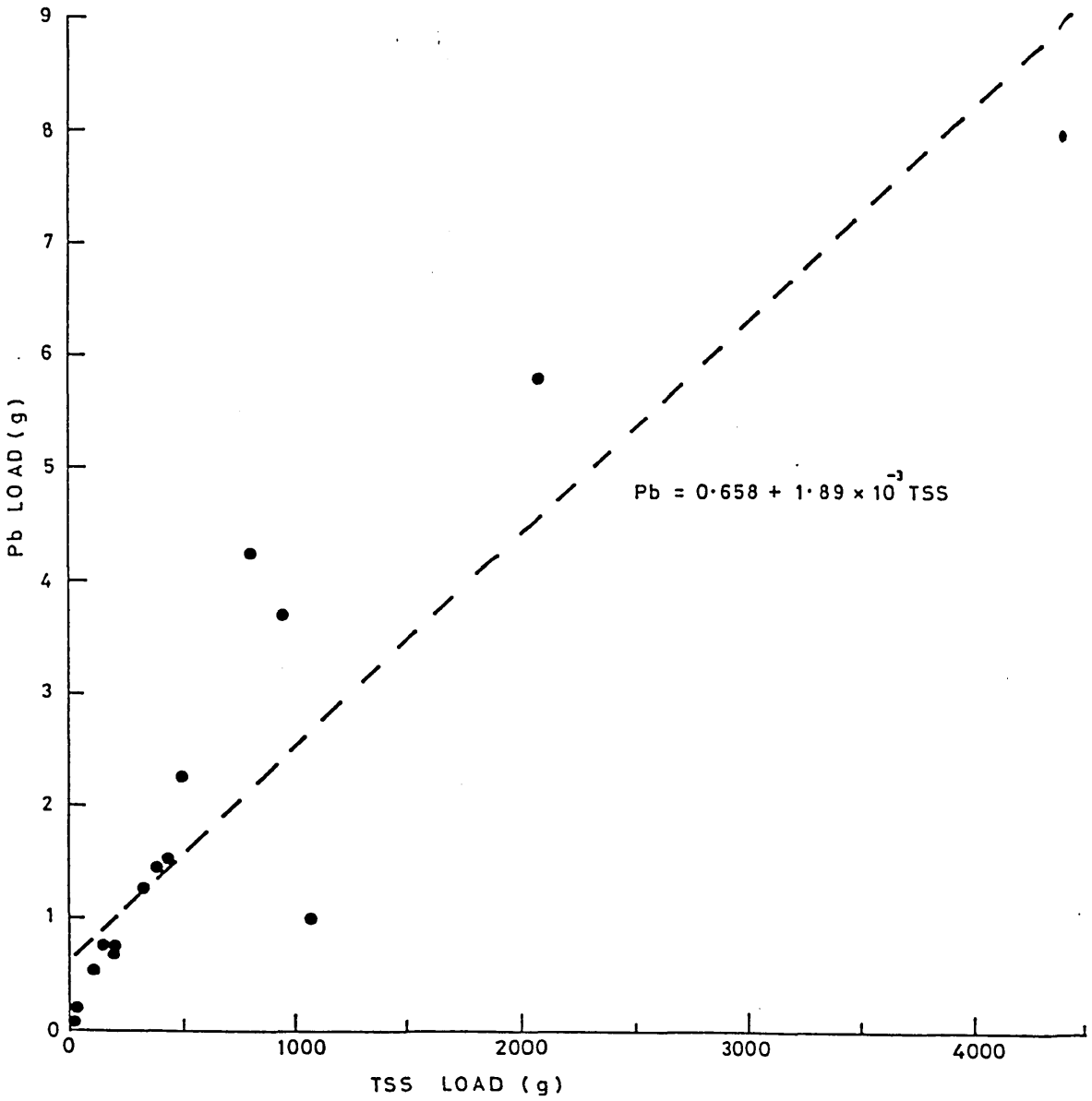



Figure 5.22 Relationship between Pb loads and TSS loads.

(b) Particle Size Distribution

Following oil extraction and particle size separations on the sieve solid samples as described in Section 5.5.4(c), the total Pb content of 50 mg subsamples from each size fraction for sampling run SS2 was determined to examine the relationship of lead content with particle size. The data are presented in Fig. 5.23A, from which it can be seen that a clear trend to higher Pb contents at lower particle sizes is evident. This can be compared with similar data (Fig. 5.24) from the two samples of road dust referred to previously (section 5.5.4(c)), from which it can be seen that contrasting trends in Pb concentration with particle size are evident. Although in general Pb concentrations in road dusts increase with diminishing particle size (Ellis and Revitt, 1982), contrasts similar to those evident in Fig. 5.24 have been reported by other workers (Biggins and Harrison, 1980) and may reflect the difficulty of sampling this type of material in a truly representative way, as noted by Hamilton et al. (1984). In the light of this, the general uniformity of the trends evident in Fig. 23A suggests that the runoff process effectively mixes the dry surface dust on the catchment to eliminate spatial variations and produce more homogeneous sieve solid samples. When both the particle size distribution of Pb concentrations and the total mass of solids found on each sieve are taken into account, however, the total mass of Pb associated with the size range studied is more evenly distributed (Fig. 5.23B), and points to the need to consider particle removal over as wide a range as possible when runoff treatment system design is being considered (section 7). Lead content was also determined for the sieve solids from sampling runs SS4 and SS6, but without prior sieving. Data obtained are presented in Figures 5.25A and 5.25B; similar trends to Figures 5.23A and 23B are evident, but are probably blurred in comparison by particle agglomeration. This was also evident in more limited data of this kind presented by Pope et al. (1978a).

Sources of Pb in the catchment are examined in detail in Section 6 in conjunction with the Br studies, but essentially the only significant sources at the site are motor vehicle emissions and possibly lead-contaminated dirt and oil washed off the undersides of vehicles during runoff events themselves.

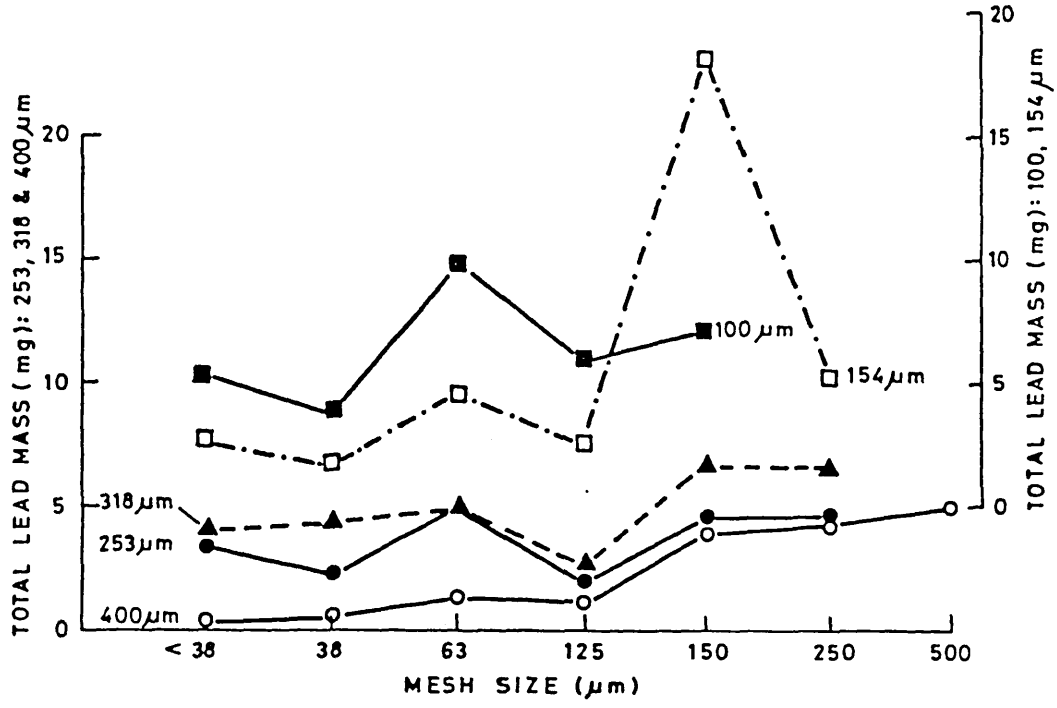



Figure 5.23B Lead load on sieve meshes (run SS2)

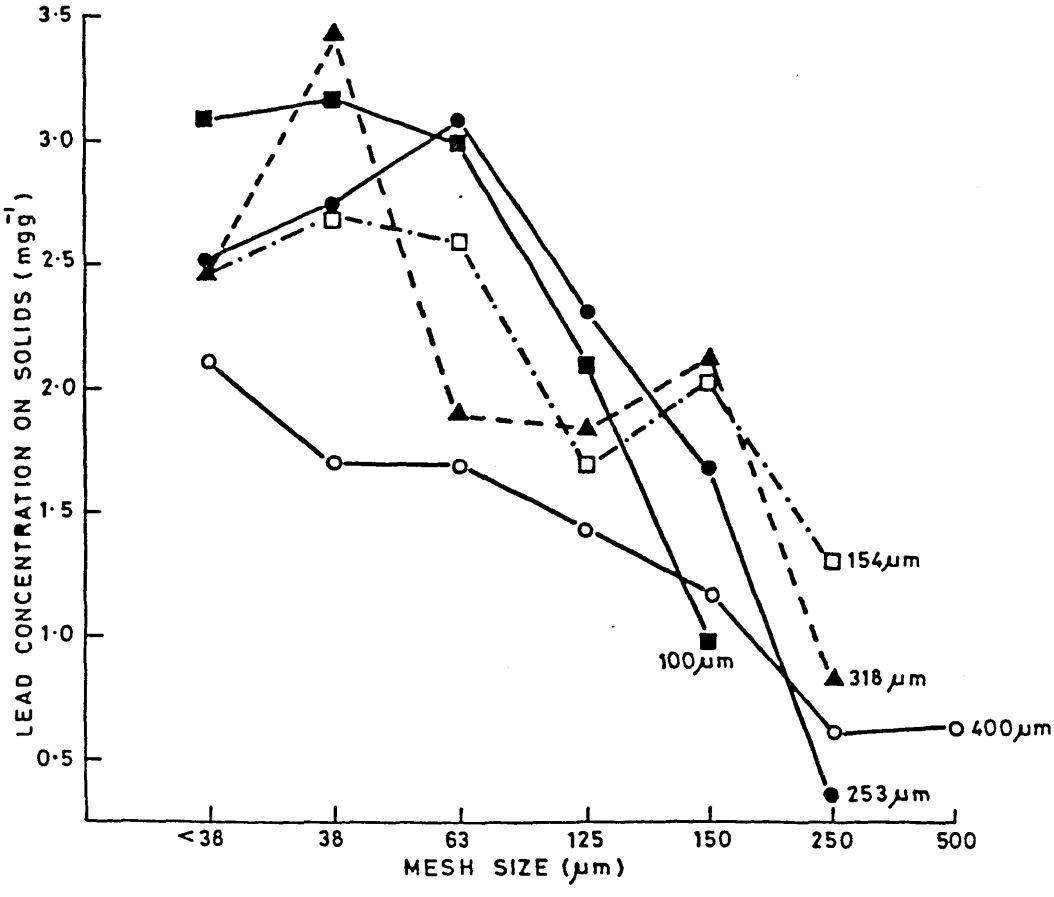



Figure 5.23A Lead concentration on oil-free sieve solids (run SS2)

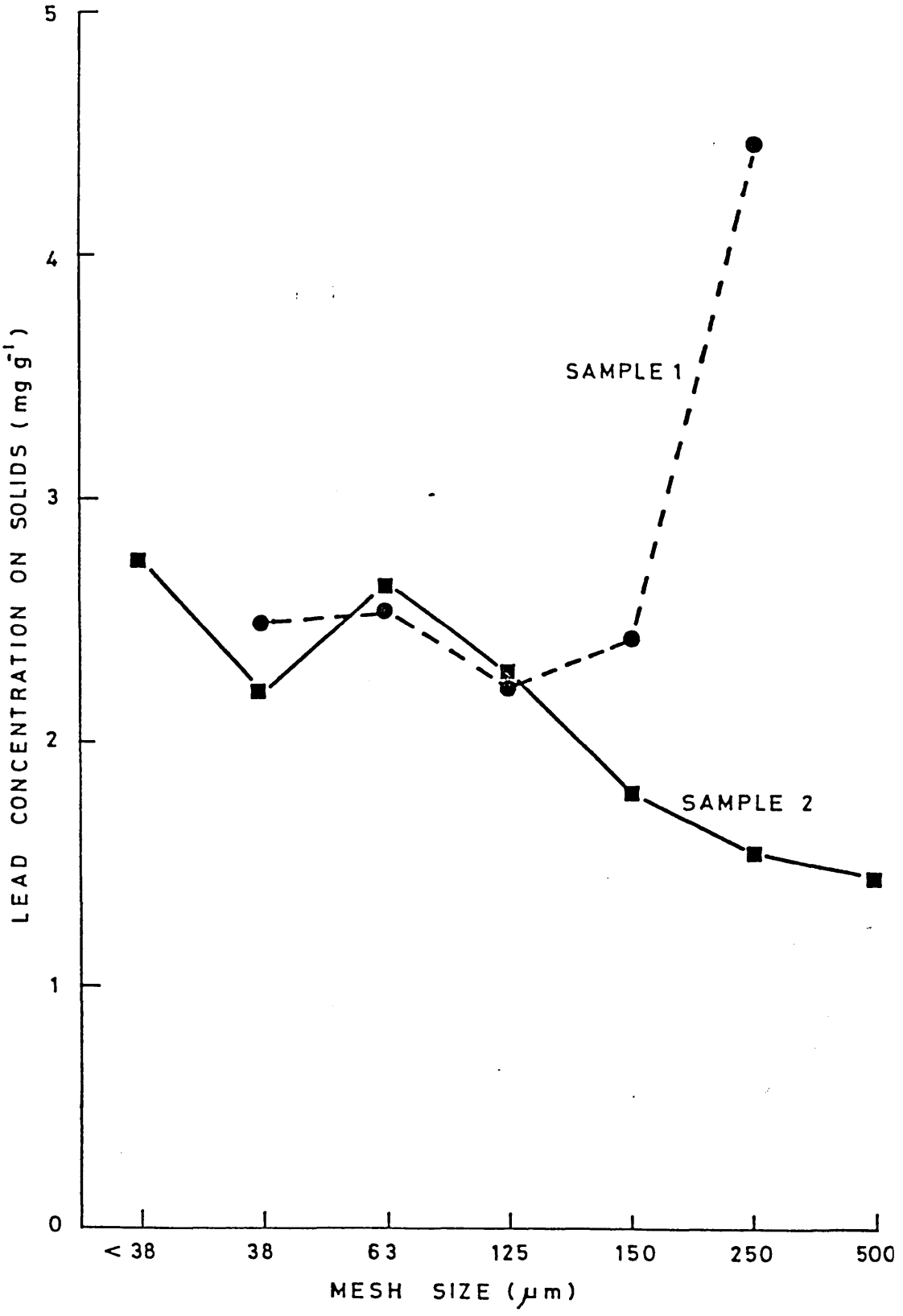



Figure 5.24 Lead concentration-particle size relationships in road dust samples

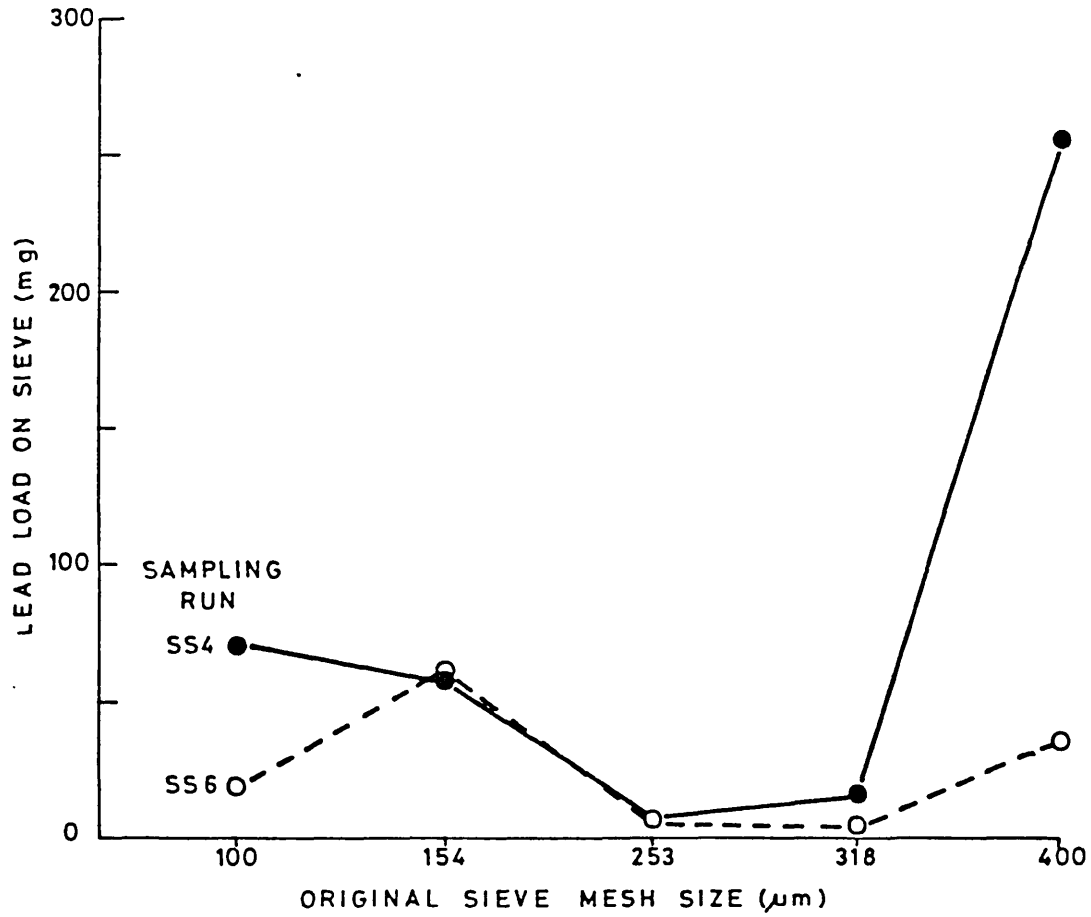



Figure 5.25B Lead load on sieve meshes (runs SS4 and 6)

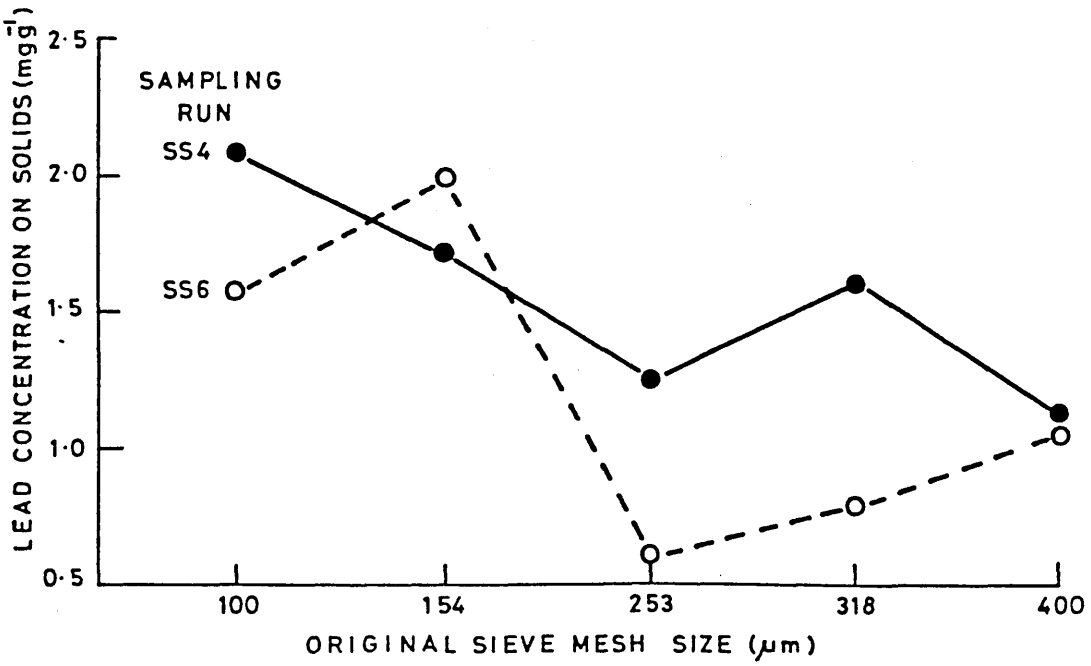



Figure 5.25A Lead concentrations on sieve solids (runs SS4 and 6)

### 5.5.6 Zinc

#### (a) General Summary

Zinc FWM data is presented in Fig 5.26. As with Pb, no statistically detectable difference in seasonal means is present, but unlike Pb there is no clustering of summer events at the upper end of the curve.

From the investigation of storage effects on metal solubilization previously referred to (Ofori, 1984a) it was clear that storage did not have a significant effect on the percentage of solid-associated Zn. Thus the greater degree of Zn solubilisation than for Pb, which is clear from Fig. 5.26, in general reflects conditions in runoff itself. Since Zn is more commonly found in soluble form, its removal in runoff from the carriageway will be less closely associated with TSS than for Pb, which may explain the different annual distribution of FWM values from that of Pb.

#### (b) Sources of Zinc

Zinc is widely found as a trace element in the natural environment and a background contribution to concentrations found in the runoff samples has to be considered. Pope et al. (1979) analysed total deposition samples at the present site and found a sharp decrease in mean Zn concentrations from 800 $\mu gl^{-1}$ at 1 m from the carriageway to 430 $\mu gl^{-1}$ at 3 m, clearly indicating that the motorway is a substantial source of Zn in runoff. No data was available for sampling positions further from the road, however, but the value of 85 $\mu gl^{-1}$ in total deposition given by Cawse and Pierson (1972) for a rural location in the UK appears to be a realistic guide to ambient background concentrations at the M1 site in the light of the data from Pope et al. (op. cit.). Comparison of this value with Fig. 5.26 shows that the background contribution to runoff Zn concentrations is significant only for one or two events at the lower end of the concentration range.

As noted in section 1.1.2, the two main highway-related sources of Zn acknowledged in the literature are the Zn content of tyre rubber and Zn-based lubricating oil additives such as Zn dithiophosphates

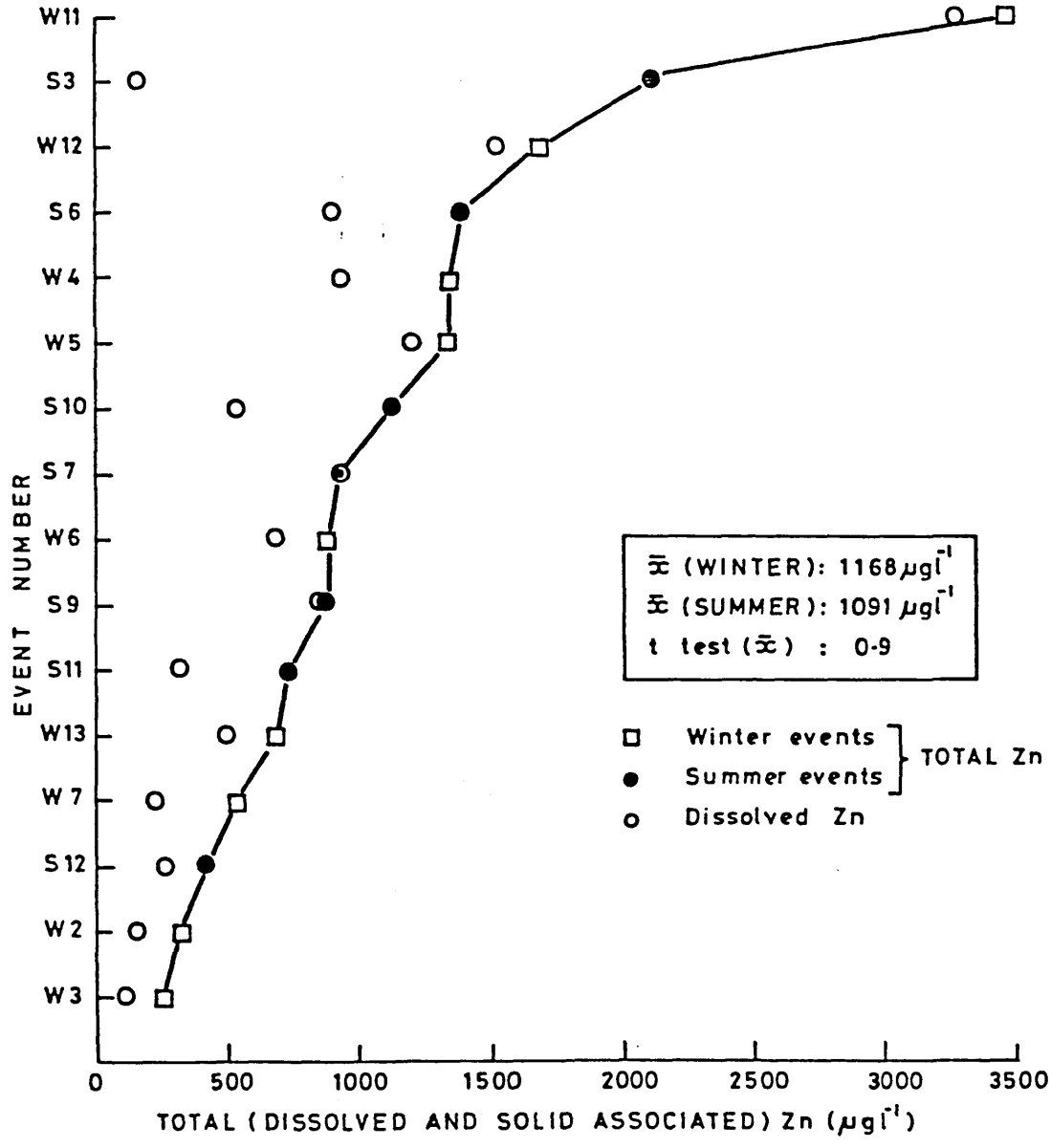



Figure 5.26 Total Zn FWM concentrations

(Lagerwerff and Specht, 1970). Analysis of seven samples of tyre rubber collected at the site gave a mean Zn content of 1.6% (SD 0.1%), a figure which is in good agreement with data given by Hedley and Lockley (1975) and Christensen and Guinn (1979). Tyre wear thus appears to be a potentially substantial contributor to runoff Zn loads, so an estimate of this contribution in the present work was made as follows:

(i) A tyre wear rate of 30 mg rubber $tyre^{-1}km^{-1}$ given by Cadle and Williams (1978) was assumed, and each vehicle was assumed to have only four tyres, giving a wear rate of 120 mg rubber $km^{-1}$ $vehicle^{-1}$.

(ii) The wear rate was multiplied by the total antecedent dry period traffic (ADPT) figures in Appendix 3 and adjusted for the length of the catchment to give a value for the rubber lead deposited in the dry period before each event, assuming no dispersion.

(iii) The resulting figures were summed and multiplied by the average tyre Zn content given above (1.6%). This was then compared with the sum of runoff Zn loads (from Appendix 5). To reduce uncertainties arising from partial sampling of some events, ADPT and Zn data for events with less than 70% of the total volume sampled (W5, 6, 13 and S11) were not included.

This procedure gave an estimated tyre-derived Zn load of 198 g for the events included, or 798% of the total runoff load of 24.8 g. The uncertainties in the figure of 198 g are considerable, due in part to possible effects of dispersion and the approximate nature of the tyre wear rate used - other authors have quoted rates of 60 (Raybold and Byerly, 1972) and 90 mg $km^{-1}tyre^{-1}$ (Dannis, 1974) - but the magnitude of the difference from recorded runoff loads is sufficient to indicate very clearly that tyre wear is the predominant source of Zn in runoff. Additional confirmation of this was presented by Christensen and Guinn (1979), who compared Zn loads in runoff from an urbanised catchment in California with estimated total tyre-derived Zn deposited between runoff events on roads within the catchment. Good agreement between runoff loads and estimated Zn deposits were found, although only two storms were studied. Apart from this limited study,

however, very little work appears to have been done elsewhere on this topic.

The possible contribution of Zn additives in lubricating oils to runoff loads has also recieved very little attention, and no attempts appear to have been made to quantify this source. In the absence of other suitable data, the data for runoff sediment oil content given in Section 5.5.9 offers the best route to an order-of-magnitude estimate of this source. Data presented in that section show that oil concentrations in runoff could be as high as 50 $mgl^{-1}$. The Zn content of lubricating oils lies in the region of 0.1% (Pierson and Brachaczek, 1974) so assuming that the bulk of oil in runoff arises from this source and contains most of its original Zn content, this would suggest that the associated Zn concentrations in runoff could be as high as ~50 $\mu gl^{-1}$. This would not appear to make it a potentially significant source in the light of the Zn concentrations found. The relative contributions of tyre wear and oil losses to Zn in runoff must at present, however, remain a matter of conjecture.

The mean Zn content of the de-icing salt samples analysed (15.5 $mg\ kg^{-1}$, Table 5.6) suggest that this was not a significant source of Zn in winter runoff. To confirm this, an estimate of the total de-icing salt contribution to the total winter Zn load was made, using an identical procedure to that used for estimating the de-icing salt TSS contribution (5.5.4(b)). A figure of 2.4% was derived, confirming that this is not an important source of Zn in runoff.

### 5.5.7 Cadmium

Summer concentrations in individual samples were usually less than 10 $\mu gl^{-1}$, so analyses for this element were eventually discontinued. Sufficient FWM data is not therefore available to justify graphical presentation, but a summary of FWM values found during winter and summer is given in Table 5.8. Apart from one unusually high winter FWM (76.0 $\mu gl^{-1}$), all remaining values were below 30 $\mu gl^{-1}$. This range is comparable with that of 0.5-9.0 $\mu gl^{-1}$ given by Dauber *et al.* (1978) and 3-6 $\mu gl^{-1}$ from Klein (1982). The FHWA (1981a) reported an annual mean of 68 $\mu gl^{-1}$ and range of 10-400 $\mu gl^{-1}$. These higher concentrations may be partially due to the urban location of the site in question. Data from Pope *et al.* (1979) and Cawse and

Pierson (1972) suggest that background deposition concentrations are usually less than 2 $\mu gl^{-1}$ in UK rural areas, so in general this is probably not a substantial contributor to runoff levels. In the great majority of samples, 80% or more of Cd was in the dissolved form.

TABLE 5.8 : Summary of cadmium FWM concentration data

| | Winter | Summer |
|---|---|---|
| Mean ($\mu gl^{-1}$) | 24.6 | 12.2 |
| RSD (%) | 99 | 51 |
| n | 7 | 3 |
| Range ($\mu gl^{-1}$) | 1.4-76.0 | 7.0-19.1 |

RSD = Relative standard deviation
FWM = Flow-weighted mean
n = number of samples

The highest FWM value (76 $\mu gl^{-1}$) arose from the winter event with the highest $Cl^-$ FWM (W11). From the data in Table 5.6, it is not possible to rule out de-icing salt as a source of Cd, in view of its low concentrations in runoff. As with Zn, an estimate of the maximum salt-derived Cd load was made for winter events using the maximum de-icing salt concentration of 2 mg $kg^{-1}$ given in Table 5.6. This was found to give a figure of 31% of the total Cd loads in the events considered, so some contribution from salting may be possible, but it would clearly not be dominant. It is probable that any Cd in de-icing salt arises because of its geochemical association with Zn in the form of an impurity (Lagerwerff and Specht, 1970). Cadmium concentrations in winter runoff may also be affected by increased mobilisation due to the high salt levels; this topic is discussed in more detail in section 5.6.3(d) in relation to Zn behaviour in winter events.

Lagerwerff and Specht (1970) suggested that Cd may be an impurity in the Zn-based lubricating oil additives previously mentioned (5.5.6(b)), again due to its geochemical association with Zn. They reported Cd levels of 0.20 to 0.26 ppm in samples of motor oil, and also tyre rubber concentrations of 20 to 90 ppm. In the present work, analysis of seven tyre rubber samples gave a range of <3 to

24 ppm. On the basis of a mean tyre rubber content of 12 ppm, an analogous calculation to that for tyre-derived Zn loads (section 5.5.6(b)) gave a 51% contribution from this source to recorded runoff loads, but without taking any dispersion etc. into account. In general, little attention appears to have been given in the relevant literature to quantifying sources of Cd in highway runoff, perhaps due to its generally low levels.

5.5.8 Chemical Oxygen Demand

The FWM data are presented in Fig. 5.27. Very few similar data for UK motorway locations are available for comparison. Cathelain et al. (1981), however, reported an annual FWM mean of 79 $mgl^{-1}$ (range 23-394 $mgl^{-1}$) from their French study, figures which are in good agreement with the present work. No mention was made of seasonal differences. The FHWA (1981a) study reported a winter mean and range of 471 $mgl^{-1}$ and 158-1058 $mgl^{-1}$ respectively, with corresponding summer values of 105 $mgl^{-1}$ and 5-226 $mgl^{-1}$, but no reason for the noticeably higher winter concentrations was advanced. Figure 5.27 and the t-test result therein makes it clear that no significant seasonal differences were found in the present work.

No directly comparable background deposition COD data are, to the author's knowledge, available for rural sites in the UK. Harrop (1983), however, quotes a range of 9-64 $mgl^{-1}$ for rainfall at various sites in US urban areas. Deposition in a rural area could be tentatively assumed to contain lower concentrations and thus not be an important source of COD for most events in the present work.

Biochemical oxygen demand (BOD) analyses were not carried out in the present work, but in other studies where both COD and BOD data have been obtained, a high COD/BOD ratio has been widely observed (Sartor and Boyd, 1972; FHWA, 1981a). The FHWA report noted that this had been partly attributed to the suppressive effects of toxic materials in runoff (e.g. heavy metals) on the bacterial processes involved in the BOD test, but that the main reason was the predominance of non-biodegradable organic materials in this type of sample, such as tyre rubber dust and oil. While the COD determination gives an indicator of the presence of such materials in highway runoff however, no conclusions can be drawn about the separate components

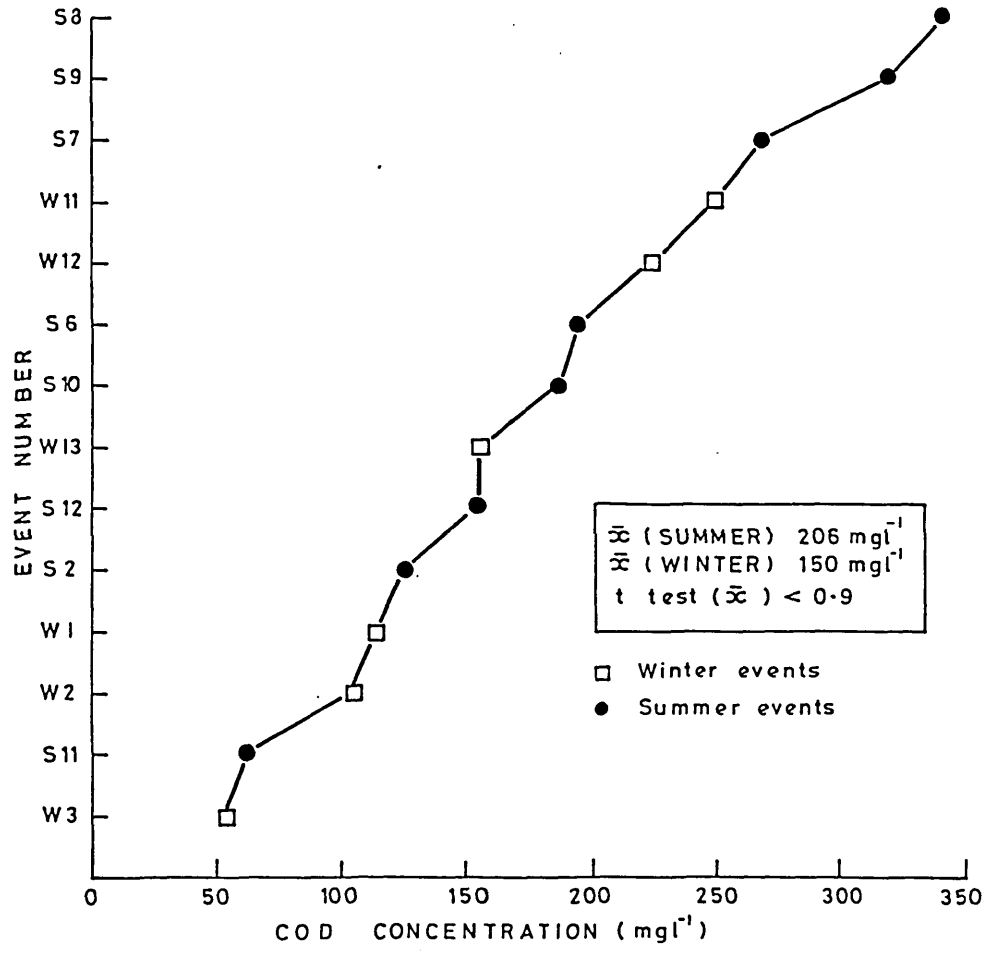



Figure 5.27 Chemical oxygen demand FWM concentrations

contributing to this oxygen demand. In this context, a limited series of experiments to determine runoff oil content were carried out in the present work, as described in the following section.

### 5.5.9 Sediment Associated Oil and PAH

#### (a) General

A limited survey of the sediment-associated fraction of these contaminants was undertaken using a number of sieve solids samples. Preliminary experiments were carried out to determine the number of extractions necessary using the flask shaker method (section 3.8.2(c)) to complete oil removal and to compare the overall efficiency of this method with the Soxhlet technique (section 3.8.2(d)). Four extractions were found to be necessary and the technique was comparable with the Soxhlet method (Appendix 8).

#### (b) Oil Content

Sieve solid samples (2 g per sieve mesh) from sampling runs SS2, SS4 and SS6 (Appendix 7) and a sample of road dust (2 g) were analysed for oil content using the flask shaker method. Samples from the 1600 μm meshes were considered as litter and were not analysed.

Figures 5.28A and B present the results of these analyses. From Fig. 5.28A, it can be seen that the highest concentration for each sampling run was found on the 253 or 318 μm sieve mesh contents, but when the weight of solids on each sieve is taken into account, the oil load is generally more evenly spread over the five meshes (Fig. 28B). The average concentrations for each run are given in Fig. 28A along with the result of the road dust analyses. The difference between the sieve solid means is probably due to antecedent conditions and storm characteristics during sampling runs, but the range of concentrations is comparable to those reported for two storms (180-400 $gkg^{-1}$) by Pope *et al.* (1978a), although these values are somewhat higher than those reported here.

The significantly lower road dust oil content (Fig.5.28A) compared with the sieve solids suggests that some oil exists as a film on the road surface during dry periods (combined with tyre rubber dust, bitumen etc.), which is then removed during runoff and subsequently

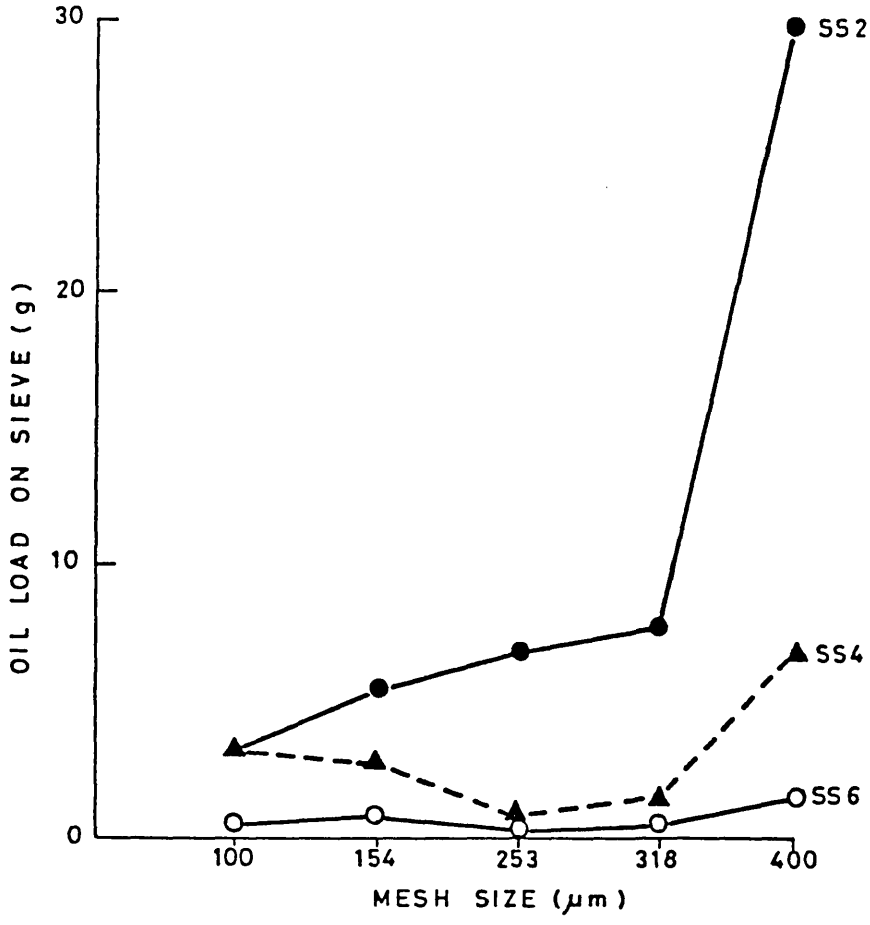



Figure 5.28B Oil load on sieve meshes

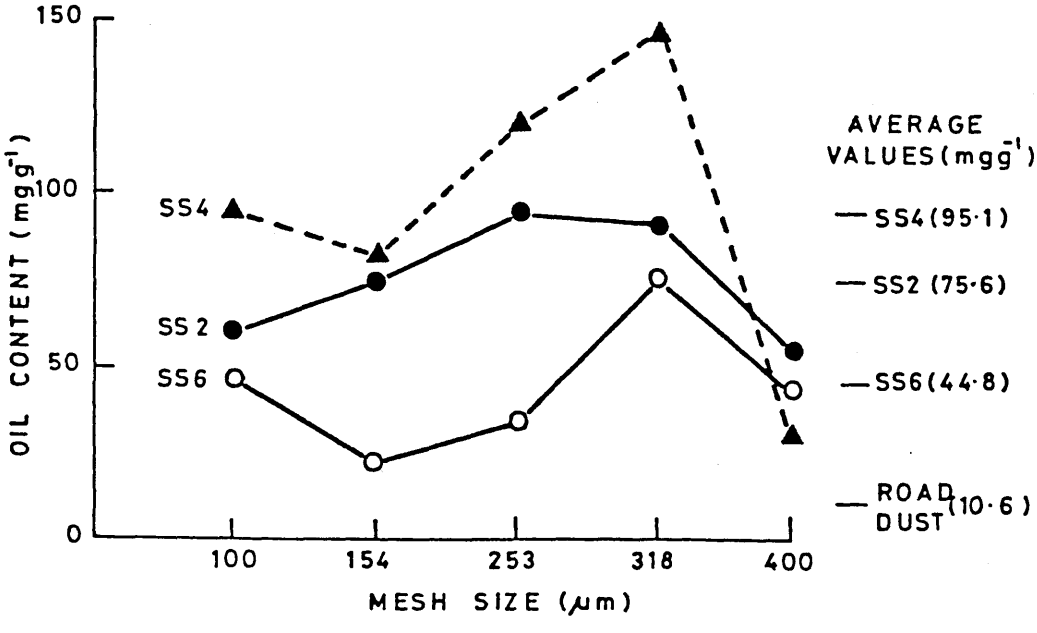



Figure 5.28A Oil concentrations on sieve solids

combines with more discrete surface dust particles to give the higher oil content subsequently found in sieve solids. The effect of oil removal on sieve solids particle size distributions to give distributions closer to that in road dust (previously noted in section 5.5.4(c)) is additional evidence for this. It is also necessary to recall in this context that the road dust samples were collected from the hard shoulder, where direct oil deposition is of course minimal compared to the travelling lanes.

Comparison of the overall sieve solid oil content mean (72 mg $g^{-1}$) with the TSS FWM data (Fig. 5.13) suggest that the range of solid-associated oil concentrations in runoff lies in the region of 2-50 $mgl^{-1}$. Pope et al. (1978a) reported that ~90% or more of oil in motorway runoff was solid-associated, however, so applying this value to the above concentrations gives an estimated range of total oil concentrations in the present work of 2-56 $mgl^{-1}$. This is comparable to concentrations reported by Pope et al. (1978a,b), Dauber et al. (1978) and the FHWA (1981a). Apart from the work by Pope et al. (op. cit.) and the present work, however, very little work appears to have been reported by other workers on the particle size distribution of sediment associated oil in motorway runoff.

(c) PAH Content

Following the oil content determinations for sieve solids and road dust, extracts were analysed for PAH as previously described (section 3.8.4). The six PAH examined (B(b)F, B(k)F, B(a)P, B(ghi)P, F and IP) were those designated by the World Health Organisation (WHO) as representative compounds for all PAH with respect to WHO drinking water standards (WHO, 1971). The results are shown in Fig. 5.29, along with literature data for a PAH analysis of used motor oil for comparison. The concentrations of individual PAHs in sieve solids ranged from 0.5 µg $g^{-1}$ to 17.9 µg $g^{-1}$ (dry weight), while the total concentrations ranged from 11.6 µg $g^{-1}$ to 43.4 µg $g^{-1}$, and it is clear from Fig. 5.29 that the concentrations of F, B(a)P and B(b)F in sieve solids are usually substantially higher than the remaining compounds, with F concentrations generally being the highest. Variations in total concentrations between sampling runs are probably due to differences in storm characteristics and antecedent conditions, as with

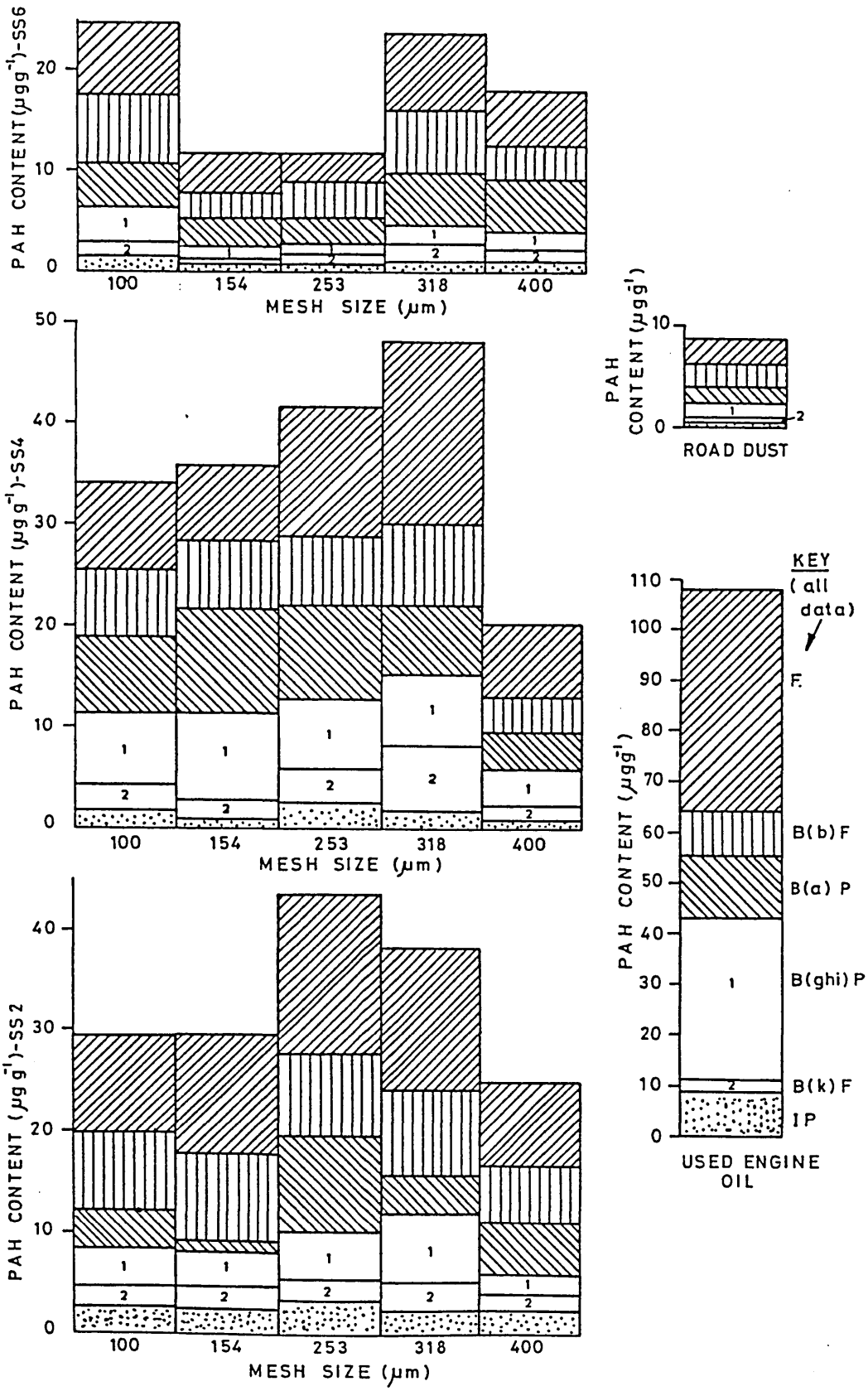



Figure 5.29 PAH content of sieve solids

oil. Associations with particle size are clearly varied but peak values on the 318 μm mesh are quite common. Figure 5.30 shows that, as with oil, the particle size distribution within runoff must be taken into account when considering mass transport, and the 400 μm size range is clearly as important as smaller sizes in this respect. The noticeably lower PAH concentrations in road dust (Fig. 5.29) compared with sieve solids suggests that the oil/rubber dust/bitumen film referred to in the previous section (5.5.9(b)) has a higher PAH content than discrete particles collected on the hard shoulder, but combines with these during runoff to give a higher PAH content in sieve solids. Nonetheless, the road dust PAH concentrations are still between two and three orders of magnitude higher than those found by Maoza (1979) in background soil samples in the site area.

In spite of the apparent lack of a strong relationship between PAH content and particle size, the total PAH/oil ratios found on the sieve solids fell within a fairly narrow range, which was within the same order of magnitude as the values for road dust and used engine oil (Table 5.9). Figure 5.29 also shows that the general pattern of occurrence of the six PAHs is similar in all three types of sample. This suggests that, in addition to exhaust emissions, loss of lubricating oil from vehicles could also be a significant source of PAH in runoff sediment and road dust.

TABLE 5.9 : Summary of PAH/oil ratios

| Sample Type | PAH/Oil Ratio ($\times 10^{-3}$) |
|---|---|
| Sieve Solids: | |
| Run SS2 | 0.44[a] (range 0.39-0.48) |
| Run SS4 | 0.42[a] (range 0.32-0.65) |
| Run SS6 | 0.42[a] (range 0.30-0.53) |
| Road Dust[b] | 0.80 |
| Used Engine Oil[c] | 0.11 |

[a] = Mean value excludes 1600 μm mesh i.e. n = 5
[b] = Single sample
[c] = From McIntyre *et al.* (1981)

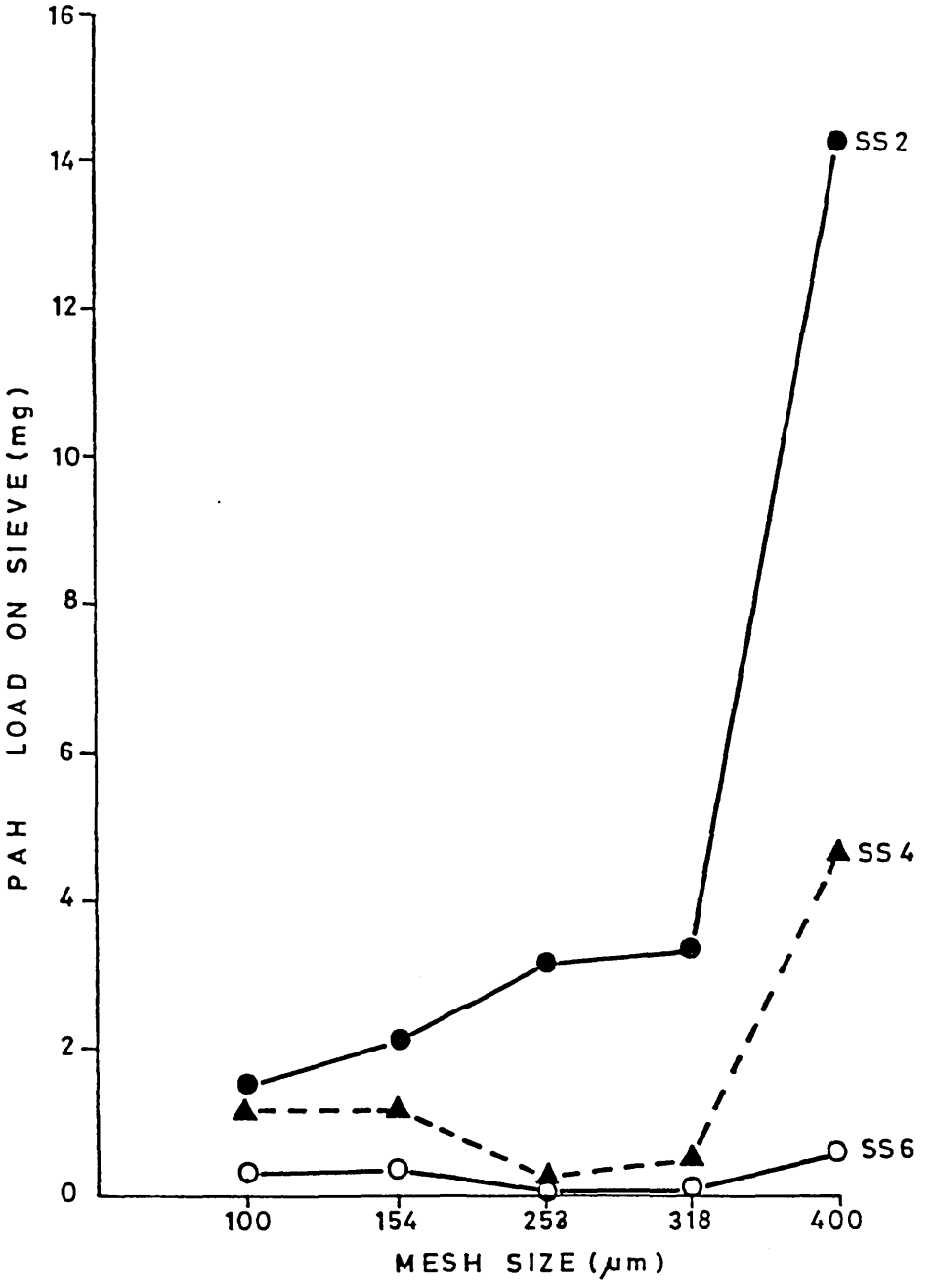



Figure 5.30 PAH load on sieve meshes

The contrast between road dust and sieve solid PAH data in Fig. 5.29 indicates that no substantial loss of PAH in the soluble form takes place during runoff. This is in agreement with the work of Pope et al. (1978a) and Klein (1982) who found that in the region of 85% of total PAH concentrations were solid-associated in motorway runoff. In view of this, and the generally narrow range of PAH/oil ratios found in the sieve solids (Table 5.9), the overall mean sieve solid oil/PAH ratio ($0.43 \times 10^{-3}$) can be used in conjunction with the estimated range of solid-associated oil concentrations derived previously (2-50 $mgl^{-1}$) to give an approximate solid-associated PAH concentration range of 0.9-22 $\mu gl^{-1}$. Assuming for the purposes of this estimate that both oil and PAH are approximately 90% solid-associated, these figures are equivalent to a range of 1-24 $\mu gl^{-1}$ for total (dissolved and solid-associated) PAH concentrations. This is comparable with the range of 1.3-14.9 $\mu gl^{-1}$ for 9 PAH in a single event given by Pope et al. (1978b), while Klein quotes lower values within the same range of 2.5-3.0 $\mu gl^{-1}$.

## 5.6 Factors Affecting Runoff Loadings

### 5.6.1 Approach to Data Analysis

In the preceding section, it was noted that FWM concentrations of some of the parameters studied appeared to be affected by such factors as the length of antecedent dry period or runoff flow rates. In order to examine these trends on a more rigorous basis, the relationship between runoff loads of specific quality variables and one or more hydrological or traffic flow variables (henceforth termed "environmental variables") have been examined, employing the widely used statistical technique of linear regression analysis. For this purpose, runoff quality data has been expressed in terms of loadings throughout this section, since use of FWM concentrations in this type of analysis introduces an additional variability to the process due to variations in event volumes and hence concentrations, especially for soluble components. The overall aim of the exercise has been to gain a clearer understanding of the main interactions between environmental variables and runoff quality rather than to attempt a formal modelling exercise. Regression analyses were carried out using the "Minitab" program (Ryan et al., 1978), available on the Imperial College computer network.

### 5.6.2 Choice of Quality Parameters and Environmental Variables

To permit a realistic assessment of factors affecting runoff quality over the entire sampling period, it was only considered worthwhile examining data for parameters for which a reasonable spread of loading data over both winter and summer periods was available, and these were considered to be TSS, Pb, Zn and $Cl^-$. (Bromide data is examined separately in Section 6). Those four constituents also cover the entire range of solubilities encountered with water quality parameters. All loading data examined in this section is given in Appendix 5.

The choice of environmental variables was governed to a large extent by the trends evident in the data presented for the four parameters in Section 5.5. Thus for TSS and Pb, four in-storm parameters were examined: runoff volume during sampling (RVS), mean flow during sampling (MFDS), peak flow during sampling (PFDS) and rise time (RT) in inverse form. These variables are fully defined in Table 5.10. Antecedent dry period traffic total (ADPT) was also included since this appeared to affect $Cl^-$ concentrations to some extent. Vehicle flow during sampling (VFDS) was included to account for any major effects on runoff quality arising from this. ADPT and VFDS are also defined in Table 5.10. Duration of event was not included as a variable, its use being limited by incomplete sampling of some events due to bottler capacity being fully utilised before runoff ended.

### 5.6.3 Results of Regression Analysis

#### (a) Total Suspended Solids

Total suspended solids load data given in Appendix 5 show that values are available for 24 events. As before, however, TSS data for event S8 has been excluded from the analysis, since although it has the second highest load value, this arises largely from a single sample with a very high TSS concentration. Analyses have thus been confined to the remaining 23 events.

It was noted in Section 5.5.4(a) that in-storm parameters such as volume of runoff and flow rates appeared to have a greater effect on TSS concentrations than other factors, and, as anticipated, the variables RVS, PFDS and MFDS (although not 1/RT) showed markedly

TABLE 5.10 : Definition of environmental variables

| Name of Variable | Abbreviation and Unit | Definition | Remarks |
|---|---|---|---|
| Runoff volume during smpling | RVS (l) | Volume of runoff flowing during sampling | Usually > 85% of event volume is covered but occasionally less due to exhaustion of sampler capacity before end of event. |
| Peak flow during sampling | PFDS (l) | Self explanatory | |
| Mean flow during sampling | MFDS ($ls^{-1}$) | Volume of runoff flowing during sampling divided by duration of sampling | |
| Inverse of rise time | 1/RT ($h^{-1}$) | Inverse of time from start of runoff to peak flow | A meaure of intensity of rainfall producing runoff during the rising limb of the hydrograph. Inverse is used to give a direct relationship between high intensities and large value of this index. |
| Vehicle flow during sampling | VFDS (vehicles $min^{-1}$) | Total number of vehicles flowing during sampling divided by sampling duration in minutes | Only hourly traffic totals available, so totals for fractions of hours computed by simple proportion. |
| Antecedent dry period traffic total | ADPT (no. of vehicles) | Total number of vehicles crossing the catchment between end of preceding event and the end of the sampling period in question | Considered more relevant in principle to runoff quality than a time-based unit, but ADPT and antecedent dry period (ADP) very highly correlated (r = 0.998). |

higher correlations with TSS loads than with other environmental variables (ADPT, VFDS). Statistical data for the strongest correlations are summarised in Table 5.11 in terms of the environmental variables considered, the number of events included, the linear (r) or multiple (R) correlation coefficients and respective percentage fits ($r^2$ or $R^2$). (Detailed definitions of r, R, $r^2$ and $R^2$ are given by Davies and Goldsmith (1977). R for multiple regressions is given as adjusted for degrees of freedom, as explained in the Minitab manual (Ryan et al., 1978). This convention will apply to all values of R given in the remainder of this section.) It is clear from Table 5.11 that although correlations with single variables generally have high values of r, the best fit arises from a multiple correlation between TSS loads and RVS with MFDS, and the coefficients of both RVS and MFDS terms in the regression equation are statistically significant at P > 0.99. The equation and an illustration of the agreement between predicted and observed values are given in Fig. 5.31.

TABLE 5.11 : Summary of strongest correlations between TSS loads and environmental variables

| Correlation Number | Independent Variables | | No. of Events | Correlation Coefficients | |
|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | | $R^2(r^2)$% | R(r)* |
| 1 | RVS | - | 23[a] | 53.4 | 0.731 |
| 2 | PFDS | - | " | 84.1 | 0.917 |
| 3 | MFDS | - | " | 88.9 | 0.943 |
| 4 | RVS | PFDS | " | 83.7 | 0.915 |
| 5 | RVS | MFDS | " | 94.2 | 0.971 |

[a] = Excluding event S8

* All values of r are significant at P > 0.95

The predominance of the MFDS term in explaining the variation in the data (Table 5.11) confirms the strong influence of flow rates upon TSS concentrations noted in Section 5.5.4(a), but the inclusion of a volume term probably indicates that significant mobilisation of solids also takes place at very low flow rates, although such solids would be expected to be fine and easily suspended. It is also notable that the relatively high percentage fit obtained with this regression

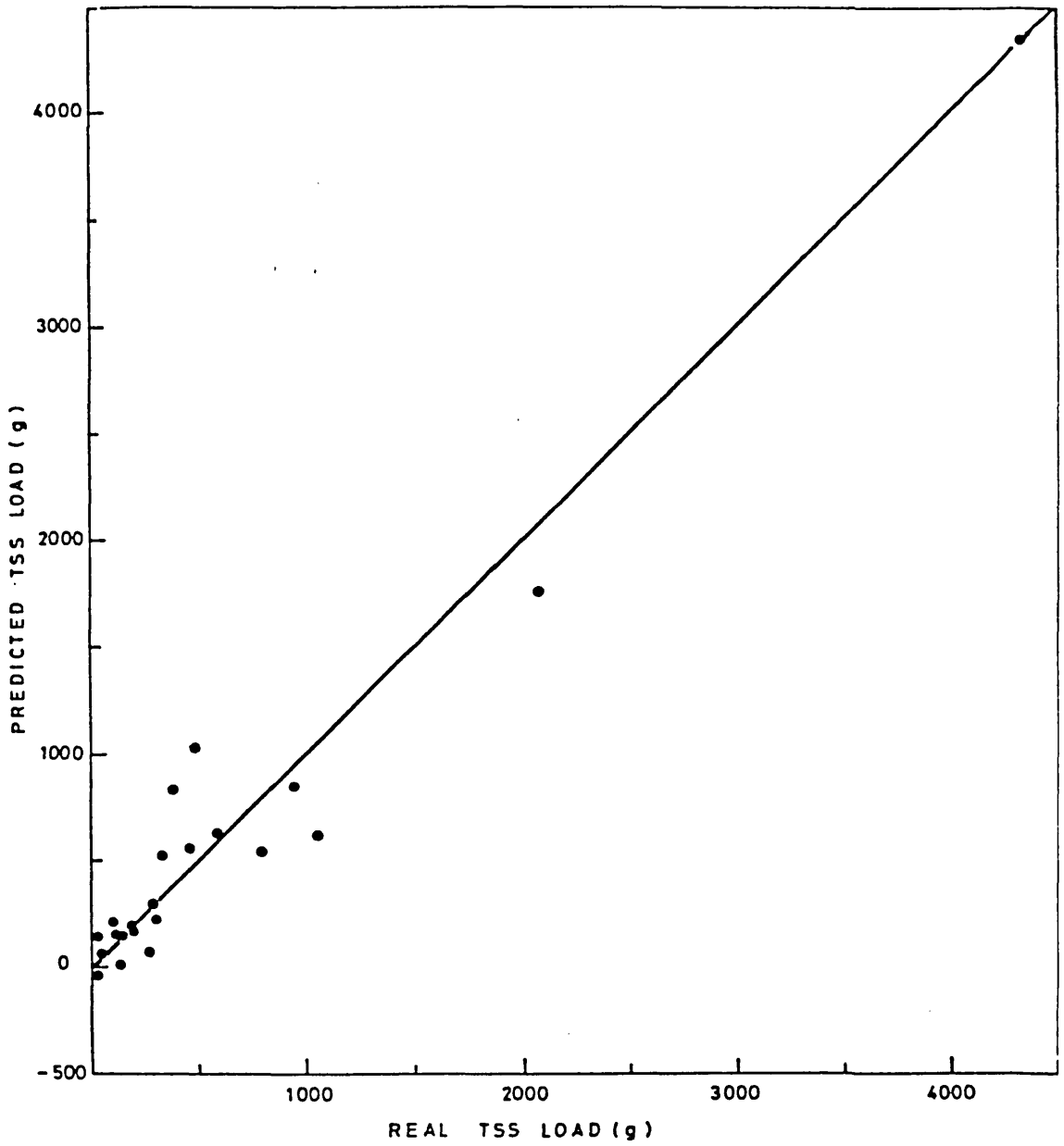



Figure 5.31 Agreement between real and predicted TSS runoff loads (Regression equation: TSS load(g) = -141 + 0.140 RVS + 1049 MFDS)

(94.2%) is based on almost equal numbers of winter and summer data. This could perhaps indicate that insoluble solids in de-icing salt do not make a sufficient contribution to winter loads to obscure the overriding dependence of TSS loads on flow rates and volumes throughout the year. Figure 5.31 illustrates, however, that the majority of loads recorded were less than 1000 g, and that the regression is clearly dominated by the highest value of 4350 g arising from a summer event. In these circumstances, a de-icing salt influence on TSS loads below 1000 g might not be easily detectable. Nonetheless, TSS and $Cl^-$ loads in winter alone showed no signficant correlation ($r = -0.052$).

The lack of correlation between ADPT and TSS loads ($r = -0.124$) indicates clearly that this is not an important factor in determining TSS loads. This implies that solids accumulate fairly rapidly on the road surface after a runoff event, but soon reach an "equilibrium" level where the rate of deposition is approximately equal to the rate of dispersion. A process of this nature was postulated by Sartor and Boyd (1972) and Shaheen (1975). At the M1 site, the main factors governing deposition are likely to be traffic flow and the rate of road surface degradation, while dispersion will probably be mainly influenced by deflation and runoff. (Street cleaning is normally an important additional dispersion mechanism, but this is very infrequent at the site, as shown in Fig. 5.8). The solids deposition data presented previously in Fig. 5.15 indicated that deflation is a major dispersion mechanism, and the degree of vehicle-generated turbulence observed at the site suggests that the equilibrium level of solids on the catchment is reached quite rapidly. Thus the solids load "deficit" caused by a large runoff event would soon be restored.

(b) Lead

As noted in Section 5.5.5(a), Pb and TSS were found to be closely associated in runoff from the site, and as expected, therefore, Pb load analysis showed very similar trends to those found for TSS. Event S8 was omitted from the analysis for similar reasons given for its exlusion from TSS analysis, leaving 16 events to be considered. A summary of the strongest correlations found is given in Table 5.12, from which it can be seen that, as for TSS, a multiple correlation

between Pb loads and RVS with MFDS gave the best percentage fit. Figure 5.32 shows the agreement between predicted and observed values, and it is clear from the diagram that the regression is less dominated by a few high values than was the case with the TSS data (Fig. 5.31).

TABLE 5.12 : Summary of strongest correlations between Pb loads and environmental variables

| Correlation Number | Indpendent Variables | | No. of Events | Correlation Coefficients | |
|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | | $R^2(r^2)$% | R(r)* |
| 1 | TSS loads | - | 16[a] | 83.7 | 0.915 |
| 2 | RVS | - | 16[a] | 73.4 | 0.857 |
| 3 | PFDS | - | " | 75.2 | 0.867 |
| 4 | MFDS | - | " | 63.3 | 0.796 |
| 5 | RVS | PFDS | " | 84.4 | 0.919 |
| 6 | RVS | MFDS | " | 86.8 | 0.932 |

[a] = Excluding event S8
* All values of r are significant at P > 0.95

(c) Chloride

Twenty-two events were available for analysis. None of the environmental variables in Table 5.10 gave a significant correlation with $Cl^-$ loads, and this is almost certainly due to the influence of de-icing salt application in the winter months. This was clearly sufficient to mask any other effects on $Cl^-$ loads when attempting an analysis on an annual basis.

A more limited analysis was thus carried out on the summer data only. The only environmental variable which gave a significant correlation was ADPT ($r = 0.643$, $P > 0.95$). A difficulty arises, however, when correlating ADPT with load values which include events only partially sampled, since, for example, two events having the same ADPT and same total load will appear to behave differently if only one event has been completely sampled. To reduce arbitrary variation from this source, therefore, all events with less than 70% of the total volume sampled were omitted from further analysis. These events were S5 and S11. The correlation coefficient between ADPT and $Cl^-$ load

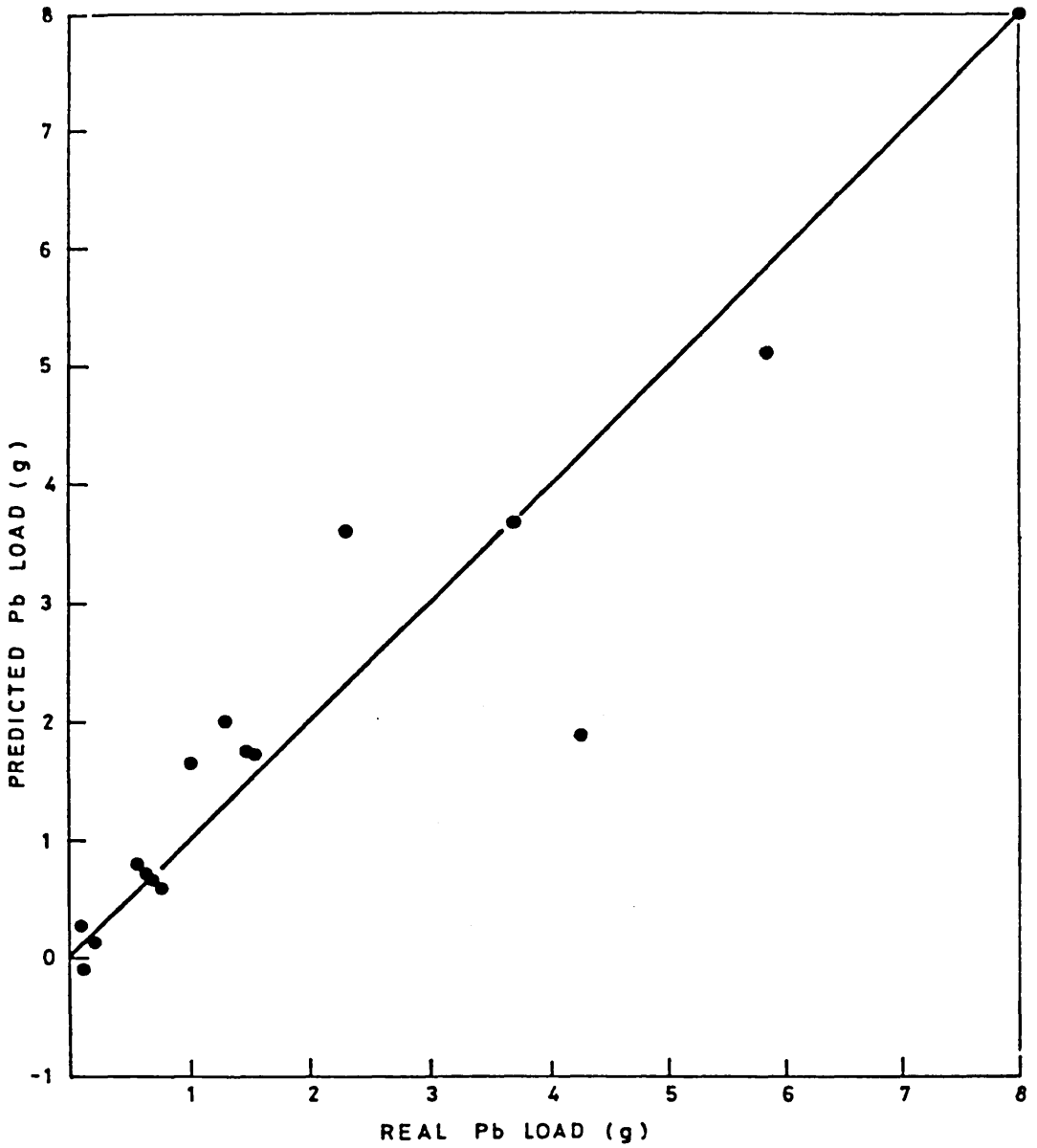



Figure 5.32 Agreement between real and predicted Pb runoff loads (Regression equation:
Pb load (mg) = -290 + 0.638 RVS + 1290 MFDS)

increased in these circumstances to 0.675 ($P > 0.95$). This correlation indicates clearly that $Cl^-$ accumulates in some way on the carriageway during dry periods. This is in contrast to the apparent behaviour of suspended solids previously discussed, and suggests that $Cl^-$ accumulates in some form which is not susceptible to deflation, possibly as a constituent of the oil/rubber/bitumen film on the carriageway which was discussed in section 5.5.9. Concerning tyre rubber, an estimate of the possible contribution to summer $Cl^-$ loads from this source was made in an analogous manner to that carried out for Zn loads (section 5.5.6(b)), using the mean $Cl^-$ concentration in tyre rubber of 705 mg $Kg^{-1}$, given in Table 6.4. Even assuming no dispersion, however, this source was only found to contribute a possible maximum of 3% of total $Cl^-$ loads for the events examined, and is clearly not significant. Compared with winter $Cl^-$ concentrations, however, those found in summer are of little importance in water quality terms.

(d) Zinc

Table 5.12 (correlations 1-6) showed that the Pb loads were highly correlated with TSS loads, RVS, MFDS and PFDS due to its high degree of solid assocation. Table 5.13 (correlations 1-6) show the results of the same correlations carried out for Zn loads, and it is clear that the association with TSS and factors affecting TSS movement is considerably less marked than with Pb. This result is in accord with the frequently high dissolved Zn concentration previously noted in Section 5.5.6(a). Although in the light of this the correlation between $Cl^-$ and Zn loads might be expected to be stronger (correlation 7, Table 5.13), a clearer picture of the relationship of Zn to TSS and $Cl^-$ emerges when winter and summer data are considered separately. Correlations 8 and 9 (Table 5.13) show that Zn loads are more closely associated with $Cl^-$ loads than with TSS in winter, while in summer (correlations 10 and 11) the situation is reversed and the association with TSS loads becomes quite marked. (For consistency with previous analyses, TSS data for event S8 has been excluded from correlation 11). In winter, therefore, Zn mobilisation appears to be assisted by the presence of high $Cl^-$ concentrations in runoff, probably due to increased competition with sodium ions for exchange sites on sediments (Feick et al., 1972; Förstner and Wittman, 1981). Lead, being much

less soluble than Zn, will be much less affected by this process, as the contrast between data in Tables 5.12 and 5.13 shows.

TABLE 5.13 : Correlations between Zn loads and other variables

| Correlation Number | Indpendent Variables | | No. of Events | Correlation Coefficients | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | | $R^2(r^2)$ (%) | R(r) | Significance of r |
| 1 | TSS loads | - | 15[a] | 39.6 | 0.629 | >0.98 |
| 2 | RVS | - | 16 | 23.2 | 0.481 | 0.9-0.95 |
| 3 | PFDS | - | " | 31.2 | 0.558 | >0.95 |
| 4 | MFDS | - | " | 28.3 | 0.532 | >0.95 |
| 5 | RVS | PFDS | " | 13.8 | 0.371 | - |
| 6 | RVS | MFDS | " | 15.3 | 0.391 | - |
| 7 | $Cl^-$ loads | - | 16 | 15.0 | 0.387 | <0.9 |
| 8 | $Cl^-$ loads | - | 9 (W) | 56.9 | 0.754 | >0.98 |
| 9 | TSS loads | - | 9 (W) | 36.6 | 0.605 | 0.9-0.95 |
| 10 | $Cl^-$ loads | - | 7 (S) | 4.0 | -0.199 | <0.9 |
| 11 | TSS loads | - | 6 (S)[a] | 80.7 | 0.898 | >0.98 |

[a] = Excluding event S8

In the light of these seasonal differences in Zn behaviour, a marked difference in the values for the dissolved percentage of sample Zn content between winter and summer might be expected. Using dissolved and total Zn FWM concentrations from Fig. 5.26, mean dissolved percentage values of 70% and 61% were derived for winter and summer periods respectively. Although these figures suggest a trend to a greater degree of Zn solubilisation in winter, the difference appears to be smaller than anticipated, but the reasons for this are not clear. Nonetheless, it is clear that a considerable proportion of the Zn load can exist in a soluble form, and, in general the possibility of enhanced heavy metal mobilisation from sediments due to deicing salt appears to be of sufficient potential concern in water quality terms to warrant further study.

Although it was noted in section 5.5.6(b) that tyre rubber deposits accumulating during dry periods might account for the majority of Zn loads in runoff, no statistically significant correlation was found between Zn loads and ADPT. This may tend to confirm that Zn loads at the M1 site are governed much more by removal mechanisms in soluble or solid-associated form than by the degree of accumulation of tyre wear products during dry periods. This is to be expected if rubber deposits are sufficiently large to supply the majority of runoff loads under most circumstances.

### 5.6.4 Summary of Regression Analysis Results

It was noted in section 5.6.2 that the parameters TSS, Pb, Zn and $Cl^-$ cover the entire range of solubilities encountered with water quality parameters, and in this respect it is notable that, in the regression analyses previously presented, Zn, which displays intermediate degrees of solid-association, demonstrated correlations with both TSS and $Cl^-$ loads when considering the sampling period (winter and summer) as a whole. The rapid solubilisation of $Cl^-$ during events noted in Section 5.5.3(a) would be expected to reduce dependence of $Cl^-$ loads on storm parameters, and the correlation with ADPT rather than in-storm variables indicates clearly that, in the absence of salting, prior accumulation is a major determining factor. For TSS and closely-related Pb, this is clearly not the case, and hydrological factors are the dominant variables.

Attempts to make detailed comparisons between the results of the present work and other comparable studies are rendered extremely difficult due to differences in site characteristics, drainage systems, prevailing climate, choice of variables and methods of approach, but nonetheless some broad trends can be discerned. In contrast to the present work, Chui *et al.* (1982), in their study of highway TSS loadings, noted that these correlated well with in-storm traffic flows rather than hydrological variables. This was ascribed to the prevalence of extended, low intensity events in their study area (Washington State, USA), during which washing of dirt from vehicle underbodies took place. Subsequent contaminant transport was considered to be more dependent on kinetic energy provided by moving vehicles rather than by rainfall. This conclusion was observed to be

in contrast to the FHWA (1981c) model, which was based on data from sites with generally more intense rainfall and incorporated rainfall intensity as a major parameter for predicting runoff solids loadings. Such an example indicates the wide range of factors which must be taken into account when comparing studies of this nature.

Cathelain et al. (1981) correlated loadings of a number of water quality parameters from a length of French motorway with a variety of hydrological and traffic variables. Direct comparison with the present work is not possible since, apart from runoff volume, rainfall parameters were the only hydrological variables examined, but nonetheless overall trends generally similar to those found in the present work for TSS, $Cl^-$ and Pb appeared evident. Antecedent dry period traffic was found to affect Zn loads, which was not evident at the M1 site, but this may have been due to the much larger number of events (64) available for analysis. In contrast to the M1 site, however, the French site was much larger (~5800 $m^2$) and incorporated long conduit lengths before the sampling point, and despite transformation of variables, a much larger number of events available for analysis and the frequent inclusion of three or more variables in regressions, the clarity of the trends emerging was not outstandingly greater than in the present work. This may be evidence that the attributes of the M1 site which governed its original selection (e.g. limited area, minimal conduit lengths) are significant advantages in studies of this kind.

# SECTION 6. SOURCES AND BEHAVIOUR OF BROMIDE IN UNTREATED MOTORWAY RUNOFF-RESULTS AND DISCUSSION

## 6.1 Introduction

The work presented in this section covers three main areas. The first is a summary of the range of $Br^-$ concentrations found in runoff and an examination of the main seasonal differences. The second examines the potential sources of $Br^-$ and Pb in runoff and the processes involved in the pathways between those sources and runoff itself. The third examines the relationship between $Br^-$ and Pb in runoff and the factors affecting Br loads.

## 6.2 Bromide Concentrations in Runoff

### 6.2.1 General Summary

In common with many of the parameters discussed in section 5.5, $Br^-$ concentrations in runoff have been summarised in terms of an FWM value for each event sampled. The data (tabulated in Appendix 6) are presented in Fig. 6.1, from which it can be seen that the concentrations found ranged from 0.06 to 4.34 $mgl^{-1}$. As noted in section 1.2, many published values for natural water $Br^-$ concentrations lie in the 0.01 to 0.2 $mgl^{-1}$ range, so it is clear that for most of the events studied the $Br^-$ concentrations were considerably greater than background values.

Winter and summer FWM values were found over the entire concentration range between 0.06 $mgl^{-1}$ (S11) and 1.85 $mgl^{-1}$ (S7), but there was a clear preponderance of winter values in the upper range of concentrations, while the exceptionally high value of 4.34 $mgl^{-1}$ also arose from a winter event, W11. This value was derived from 16 individual samples with high $Br^-$ contents, rather than one or two extreme values. The tendency towards higher winter FWM values is reflected in the difference between the seasonal means (Fig. 6.1), although this is not statistically significant at $P > 0.9$. This is probably partly due to the wider spread of winter FWM values (RSD 89%) than for summer (RSD 63%). The difference between seasonal mean volumes for the events concerned (summer 13% > winter) was small and not statistically significant, so this was not a major factor causing lower concentrations during the summer.

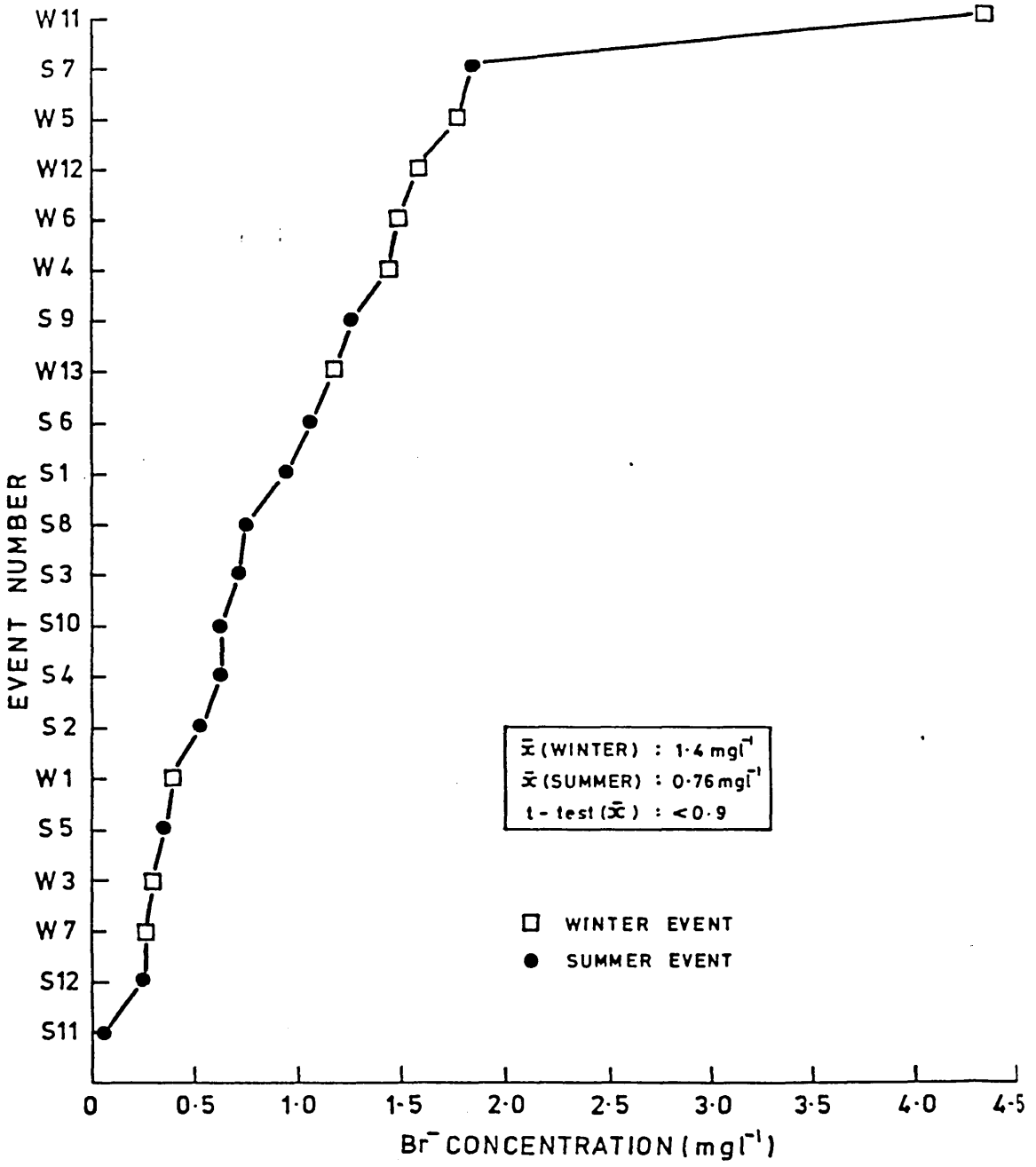



Figure 6.1 Bromide FWM concentrations

In considerable contrast to Pb (section 5.5.5), the great majority (>98.5%) of $Br^-$ (and $Cl^-$) in early analyses of runoff samples was found in the filtrable fraction. In view of this, dilution effects were expected to be a major factor in determining runoff concentrations, while a first flush effect was also anticipated in many cases, depending on the rate of $Br^-$ solubilisation. Figure 6.2 shows a storm hydrograph illustrating changes in $Br^-$, $Cl^-$ and conductivity concentrations, and as anticipated the close relationship between the three parameters is very noticeable, confirming the essentially dissolved nature of $Br^-$ in runoff. Because of this, routine separate analysis of suspended solids for $Br^-$ and $Cl^-$ was eventually discontinued, and samples were subsequently analysed without prior filtration.

### 6.2.2 De-icing Salt Contribution to Bromide and Lead in Runoff

Bromide winter FWM values were highly correlated with $Cl^-$ winter FWM values ($r = 0.974$), and this fact taken together with the trend to higher $Br^-$ FWMs in winter previously noted (section 6.2.1) strongly suggested that de-icing salt was a potential contributor to $Br^-$ loads and hence influenced FWM values. The analytical results from $Br^-$ analysis of four salt samples were given in Table 5.6 (section 5.5.3(b)), from which it can be seen that the mean $Br^-$ concentration was 230 mg $kg^{-1}$, which, solids excluded, was a far higher concentration than that found for the other contaminants examined (Pb, Zn and Cd). In view of this, an estimate was made of the de-icing salt contribution to the sum of $Br^-$ loads for all winter events analysed, in an identical manner to the procedure adopted for estimating the salting solids contribution, in section 5.5.4(b). This led to a figure of 6.33 g for the total salt contribution, or 35% of the total summed winter $Br^-$ load of 17.92 g, so clearly de-icing salt could have made a significant contribution to the total winter load recorded. In contrast, an identical exercise for Pb led to an estimate of 1.3% for the de-icing contribution to the sum of Pb loads, so this is clearly an insignificant source of Pb in runoff.

Since both $Br^-$ and $Cl^-$ in de-icing salt are both almost entirely in soluble form, the reasonable assumption can be made that there will be a close relationship between any variation in salt-derived $Cl^-$ and

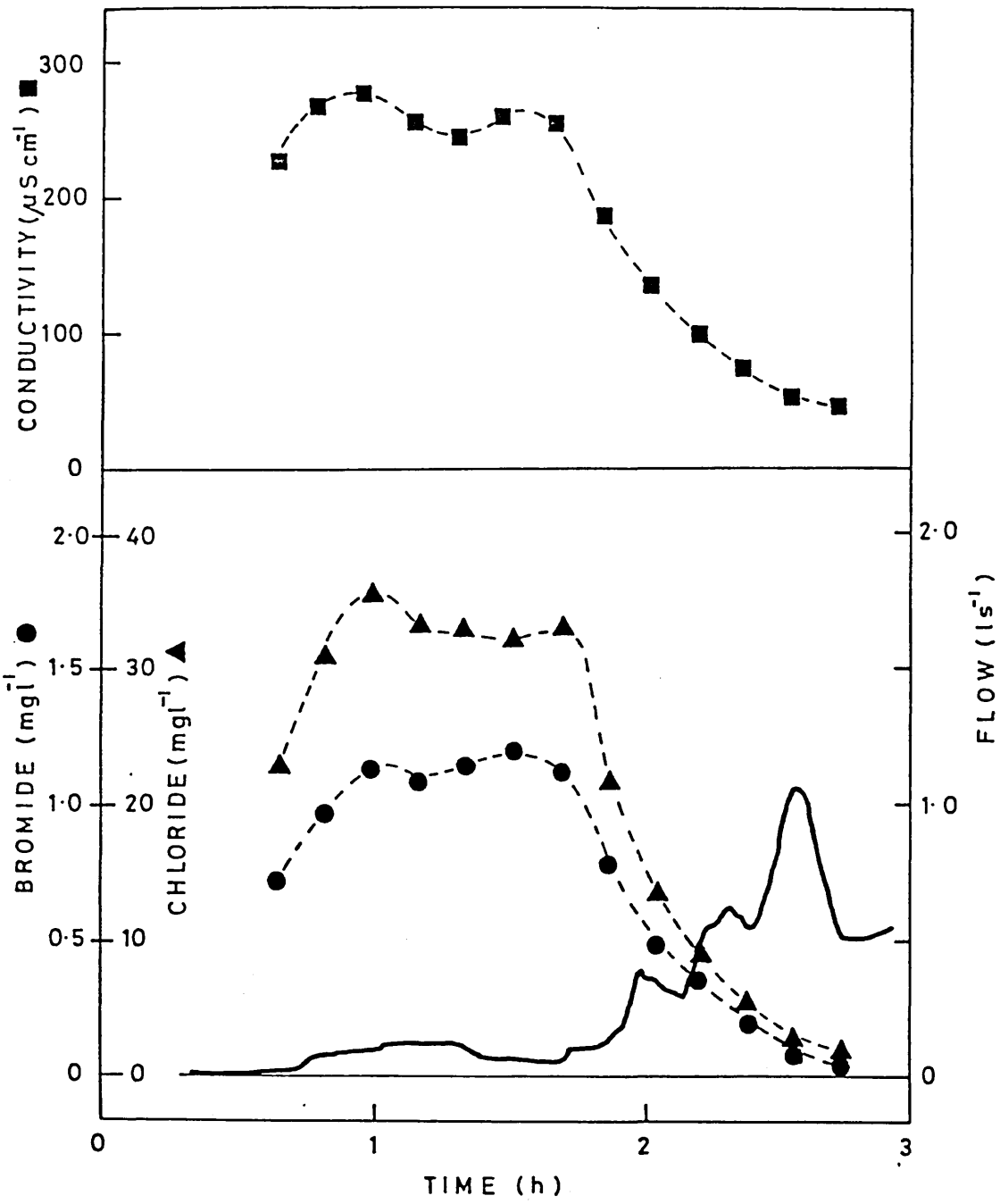



Figure 6.2 Typical hydrograph showing in-storm changes in $Br^-$ and $Cl^-$ concentrations and conductivity

$Br^-$ content in runoff. This is borne out by the strong correlation between $Br^-$ and $Cl^-$ winter FWM values previously noted. On the basis of this assumption, therefore, and following on from the calculation in the previous paragraph, a salt-derived $Br^-$ load has been estimated for each of the individual events sampled and subtracted from the total event load to give a "non-salt" $Br^-$ load and corresponding FWM in each case. The mean of these non-salt winter $Br^-$ FWM values has then been compared with the mean of total $Br^-$ winter FWM values and the mean of summer FWM values, in order to assess the effect of salting on the winter FWM data. The results of this are summarised in Table 6.1, and individual event data from which that table is derived are given in Appendix 6.

TABLE 6.1 : Comparison of $Br^-$ seasonal FWM means before and after adjustment of winter values for salting effects

| | $Br^-$ FWM concentrations ($mgl^{-1}$) | |
|---|---|---|
| WINTER (n = 9) | (not adjusted) | (adjusted) |
| Mean | 1.41 | 0.78 |
| RSD (%) | 89 | 70 |
| Range | 0.26-4.34 | 0.21-2.00 |
| SUMMER (n = 12) | | |
| Mean | 0.76 | |
| RSD (%) | 64 | |
| Range | 0.06-1.85 | |

RSD = Relative Standard Deviation

Table 6.1 shows clearly that removal of the salting influence in this manner from winter FWM values has two main effects on the data:

(a) The winter mean and RSD are both significantly reduced following adjustment.

(b) The adjusted winter mean and RSD are both much closer to the corresponding summer values.

The close agreement between the adjusted winter mean and the summer mean strongly suggest that de-icing salt was the main cause of the

trend to higher $Br^-$ FWM values in winter. The reduction in the RSD from the non-adjusted to the adjusted winter mean is therefore almost certainly due to the removal of an effectively arbitrary element of variability in the $Br^-$ load data due to the salting contribution. The similarity in adjusted winter and summer means and RSD values further suggests that the remaining causes of variation are similar and of similar magnitude during both winter and summer.

## 6.3 Non-Salt Primary Sources of Bromide and Lead in the Catchment Area

In addition to de-icing salt, three other main types of sample were analysed for Br and Pb in order to establish other major sources of these elements in runoff. The sample types were:

(i) Background deposition

(ii) Filtered ambient air

(iii) Tyre rubber and bitumen

Data for the Cl content of these samples have also been given. In the case of (i) and (ii), the range of Cl/Br ratios in deposition and ambient air at selected rural sites in the UK has been well documented (Cawse, 1981). Large divergences from such data can therefore be additional evidence for the presence of non-natural Br sources, so relevant comparisons with the present work have been made where appropriate. Sampling and analytical methods for each sample type are described in sections 2 and 3 respectively.

### 6.3.1 Background Deposition

Bromide concentration data from four samples of total deposition from the farm gauge were summarised in Table 5.3. The mean concentration found at that site, 0.02 $mgl^{-1}$, was, in comparison with the runoff FWM data in Fig. 6.1, clearly insignificant for all events except that with the lowest value, S6. Likewise, the mean Pb background concentration, 0.04 $mgl^{-1}$ (table 5.3) was also very low compared with all but the lowest FWM values (Fig. 5.21). The contrast between the background $Br^-$ and Pb deposition data and roadside values suggests clearly that the motorway is the major source of these elements in roadside deposition and hence runoff.

### 6.3.2 Ambient Air

#### (a) Element Concentrations

Fifteen filter samples were taken between February and September 1981. Sampling periods ranged between 4 and 16 days depending on circumstances. For six of the fifteen periods, between July and September, a KOH trap was also installed after the filter (Section 2.5.3, Fig. 2.18) in order to trap non-particulate Br species. Data for individual sampling runs are given in Appendix 9, but these are presented in Fig. 6.3 and summarised in Table 6.2, along with literature Pb, Br and Cl background values for comparison. The table shows that both Br and Pb particulate air concentrations are in the region of an order of magnitude higher than background values and highly correlated (r = 0.963). It is now widely accepted that in the absence of specific industrial sources of Pb (such as smelting), the principal source of particulate Pb in the atmosphere is exhaust emissions from petrol-engined vehicles using leaded fuel. Since major non-vehicular sources of airborne Pb are absent in the locality of the site, it is clear that the motorway is the major source of airborne Pb.

TABLE 6.2 : Summary of air filter data

| Element Concentration or Ratio | Mean[a] | RSD (%) | Range | Background (Reference in brackets) |
|---|---|---|---|---|
| Br ($\mu g\ m^{-3}$) | 0.59 | 56 | 0.12-1.17 | 0.027-0.076 (1) |
| Pb ($\mu g\ m^{-3}$) | 1.22 | 54 | 0.23-2.09 | 0.04 -0.23 (1,2,3) |
| Cl ($\mu g\ m^{-3}$) | 1.51 | 50 | 0.56-3.10 | 1.72 -3.92 (1) |
| Br/Pb (w/w) | 0.49 | 13 | 0.35-0.61 | 0.43 -0.67 (1) |
| Cl/Br (w/w) | 3.36 | 62 | 1.09-7.00 | 46.7 -75.0 (1) |

Least squares fit for Br and Pb data : Br = 0.005 + 0.477 Pb
Correlation coefficients : Br-Pb 0.963 ($p > 0.99$)
: Cl-Br 0.282 ($p < 0.9$)

[a] = all values refer to 15 samples (Appendix 9)
References: (1) Cawse (1981); (2) Harrison and Williams (1982); (3) Clark *et al.* (1984).

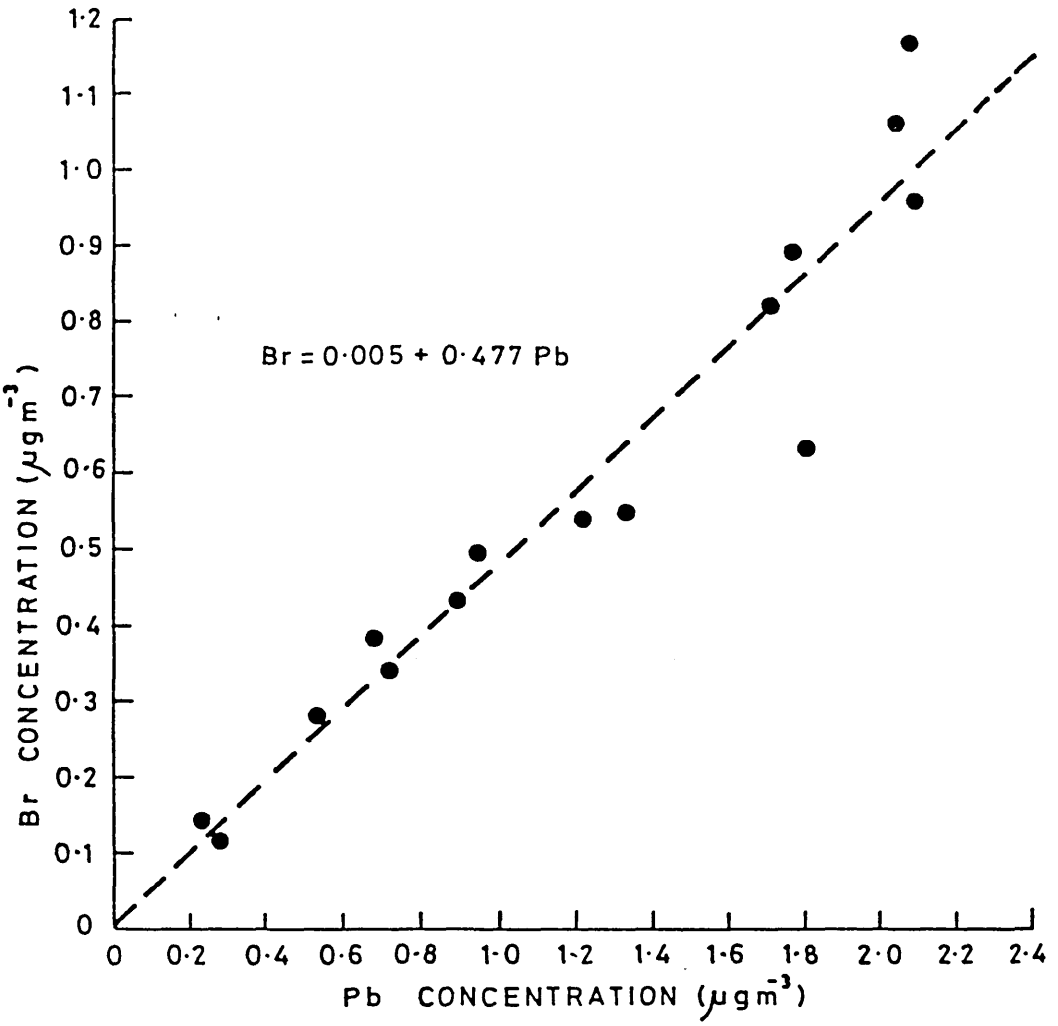



Figure 6.3 Relationship between Br and Pb in filtered air samples

All leaded fuel sold in the UK contains the additives 1,2 dibromoethane (EDB) and 1,2 dichloroethane (EDC) (Associated Octel Ltd., 1981) to act as "scavengers" to ensure the emission of Pb in an inorganic particulate form, predominantly PbBrCl (Hirschler et al., 1957; Habibi, 1973). If petrol engined vehicle emissions are the principal source of particulate Br in ambient air at the site, a close correlation between Br and Pb particulate concentrations in air would be expected, and Fig. 6.3 and Table 6.2 show that this is indeed the case. In Fig. 6.3, the intercept on the Br axis (i.e. Pb = 0) is 0.005 $\mu g\ m^{-3}$, which is less than 5% of the lowest concentration recorded and strongly indicates that the background Br concentrations are negligible in the site area. Other workers have also found very low background Br concentrations in air. Harrison and Sturges (1983b) undertook a survey of Br/Pb ratios in air in the Lancaster, UK, area and found Br intercept values between 0.001 and 0.014 $\mu g\ m^{-3}$, while Cawse (1981) reports rural values in the UK of 0.027 to 0.076 $\mu g\ m^{-3}$. Generally speaking, therefore, the non-vehicular Br background level is small compared to average concentrations found in this work, and the majority of airborne particulate Br and Pb at the site clearly arises from vehicle emissions.

Comparison of the mean Pb and Br concentrations in Table 6.2 with values from the review of Harrison and Sturges (1983a) shows that the data are realistic for the type of location, although few data are available for Br at motorway locations in the UK. Clark et al. (1984), however, who measured particulate Pb besides the M1 only 4 km NW of the runoff sampling site, found a mean Pb concentration of 1.16 $\mu gm^{-3}$, which is very close to that found in this work.

TABLE 6.3 : Bromide trap data

| Date (1981) | Corresponding filter sample run[a] | Bromide | | Chloride | |
|---|---|---|---|---|---|
| | | concn ($\mu gm^{-3}$) | % of filter (concn) | concn ($\mu gm^{-3}$) | % of filter (concn) |
| 10/7-17/7 | 9 | <0.07 | < 6.6 | <3.8 | <259 |
| 17/7-28/7 | 10 | <0.03 | < 2.6 | <1.7 | <136 |
| 3/8-12/8 | 11 | <0.05 | < 6.1 | <3.3 | <252 |
| 19/8-27/8 | 13 | <0.04 | < 9.3 | <3.8 | <413 |
| 27/8-2/9 | 14 | <0.07 | <58.3 | <6.3 | <748 |
| 2/9-11/9 | 15 | <0.05 | <14.7 | <4.4 | <365 |

[a] = see Appendix 9

Table 6.3 presents KOH trap data. For Br analysis of trap contents both blank and sample values were below the detection limit under the analytical conditions employed. The blank value was thus regarded as zero, and maximum values of "trappable" Br concentration calculated accordingly. For Cl, both the blank and the sample contents were detectable. The detection limit of the overall method was, by convention, defined as twice the blank value. By this standard, none of the sample values exceeded the detection limit, so the minimum detectable air concentration for each run has been expressed in terms of twice the blank value divided by the corresponding volume of air filtered. These minimum concentrations have also been expressed as a percentage of the filter-based concentration for the same run.

Although the trap data indicate that the method was too insensitive to provide much information on the Cl retention efficiency of the filter, the data do indicate that the retention efficiency for Br was generally satisfactory for purposes of the present work. The data also indicate that any volatile forms of Br (e.g. HBr) lost by particulates on the filter were still retained within the filter matrix. This topic is dealt with more fully in section 6.3.2 (b) following. Lead retention efficiency was not examined, but the technique used has been widely employed by others (Harrison and Sturges, 1983a) and its efficiency has also been found to be superior to other methods in tests by Colwill and Hickmann (1981).

The mean Cl air concentration (1.51 μg $m^{-3}$, Table 6.2) in contrast to Br and Pb, is very similar to the range of background values, suggesting that vehicle-related sources are not a major fraction of total concentrations, and the low correlation between Br and Cl concentrations (r = 0.282) tends to confirm this. It is possible, however, that some Cl may have been retained by the KOH trap, and that ambient concentrations are in fact higher, but the high blank value for Cl makes this difficult to assess.

(b) Element Ratios

As noted in section 1.1.2(a), the admixture of tetraakyl lead (TAL) compounds and scavengers in almost all leaded fuel sold in the UK and USA (known as "CB mix") is such that Pb and Br are present in a 1:1 atom ratio (Associated Octel Ltd., 1981) giving a Br/Pb w/w value of 0.39, referred to in the following discussion as the "ethyl ratio". As noted in the previous section, under normal working conditions, the major Pb species in exhaust gases is PbBrCl, in which the Br/Pb ratio is the same as the ethyl ratio. When vehicle traffic is the dominant source of Pb and Br in ambient air, therefore, the slope of a regression line of Br upon Pb will be expected to be close to this value. The data in Table 6.2 shows that, from the present work, the slope has a value of 0.48, with 95% confidence limits of 0.40-0.56. Thus the ethyl ratio (0.39) falls just short of the lower confidence limit, and this therefore suggests a trend to Br/Pb values greater than the ethyl ratio at the site. Although a number of studies of Br/Pb ratios in urban and suburban locations have found values lower than the ethyl ratio (Harrison and Sturges, 1983a), several studies have reported values similar to the present work from other sites alongside major highways, e.g. 0.45 (Giauque *et al.*, 1974), 0.47 (Dzubay *et al.*, 1979), 0.45 (Bullin and Moe, 1982) and 0.58 (Bullin *et al.*, 1985). While none of these authors gave detailed reasons for the high values found, Harrison and Sturges (1983a) suggested that, apart from non-vehicular background sources (which are negligible at the present site), possible causes of Br/Pb values higher than the ethyl ratio may include preferential emission of Br from vehicle exhausts in a Pb-independent form, in conjunction with retention of such forms on sampling filters. The forms emitted probably consist of organic compounds such as EDB and inorganic forms such as $NH_4Br$ (section 1.2.2(a)).

The retention of volatile brominated organic compounds by a membrane filter such as that used in the present work is not thought to be significant (Baumann and Heumann, 1985) but particulate $NH_4Br$, as found in exhaust gas samples by Li and Smith (1976), could be more easily retained. Subsequent conversion of this to HBr *via* the equilibrium reaction

$$NH_4 \rightleftarrows HBr + NH_3$$

was considered possible by these authors, and the KOH trap (section 6.3.2(a)) was installed to assess any Br in this form not trapped by the filter. Such quantities were generally negligible, however, and this is in accord with the observation of Harrison and Sturges (1983a) that most membrane materials are essentially basic and would tend to retain HBr. In addition to these considerations, it is pertinent to note that the rural location of the M1 site differs from the generally urban locations of almost all Br-Pb relationship studies previously reported. This important factor would tend to diminish both the effect of sulphate-polluted urban atmospheres in reducing ambient Br/Pb ratios previously noted (Biggins and Harrison, 1979) and the contribution of an aged Br-deficient Pb aerosol background in urban areas to overall Br/Pb ratios. Background ratios found in rural (non-motorway) UK locations by Cawse (Table 6.2) are significantly higher than many reported urban values.

In conclusion, therefore, it is clear from the air sampling data that vehicle emissions are the major course of Br and Pb found in ambient air at the site, and the mean Br/Pb ratio found is comparable to many values which have been found in other generally similar locations. Moreover, the mean Cl/Br particulate ratio is very low compared with general background values, and this is additional evidence for the motorway being the major source of Br in ambient air at the site.

### 6.3.3 Tyre Rubber and Bitumen Samples

Five separate pieces of tyre rubber were collected which, from tread pattern etc., appeared to originate from five different tyres, three from cars and two from lorries. One or two subsamples were taken from each piece. Nine pieces in total were analysed for Br and Cl and seven for Pb. For bitumen, six samples were collected in total from the edge of the hard shoulder bordering the french drain, where there is no kerb. Eight analyses were carried out for Br and Cl and seven for Pb. For both types of sample, Br content was frequently below the INAA detection limit, and similarly for Cl content in bitumen samples. Table 6.4 presents a summary of Br, Pb and Cl data for tyre rubber and bitumen, treating all subsamples on an equal basis. The Cl/Br ratio data for bitumen arises from only two samples, the first in which only the Br content was detectable (Cl/Br $<$ 7.3) and the second in which only the Cl content was detectable (Cl/Br $>$ 43.9). In the remaining samples, neither Br nor Cl were detectable, so no ratio could be calculated.

The table shows that tyre rubber is an insignificant source of Br, but the Pb content could conceivably make a significant contribution to runoff loads under some circumstances. In section 5.5.6(b), a basis for estimating the potential tyre rubber contribution to runoff Zn loads was presented, and this approach can also be used to estimate the potential tyre rubber contribution to the sum of Pb loads recorded during the sampling period. This approach showed that the maximum contribution was less than 3%, and therefore this source of Pb is of no real significance for runoff loads. As noted in section 5.6.3(c), a similar calculation carried out for $Cl^-$ in summer runoff alone led to a very similar conclusion, with less than 3% of the summer $Cl^-$ total load being derived from this source. Because of de-icing activity in winter, comparison on an annual basis would show an even more insigificant contribution.

Table 6.4 also shows that concentrations of Br and Pb in bitumen are very low, and although it is extremely difficult to quantify the individual contribution of road surface wear to runoff loads, this does not appear to be of much significance in the present work.

TABLE 6.4 : Br, Pb and Cl data for tyre rubber and bitumen samples

| Element Concentration or ratio | Tyre Rubber Samples | | | | Bitumen Samples | | | |
|---|---|---|---|---|---|---|---|---|
| | No. of Subsamples | Mean | Standard Deviation | Range | No. of Subsamples | Mean | Standard Deviation | Range |
| Br ($\mu g\ g^{-1}$) | 9 | - | - | $<5.6$ | 8 | - | - | $<9.6$ |
| Pb ($\mu g\ g^{-1}$) | 7 | 77 | 36 | 29-122 | 7 | 8.9 | 3.4 | 5.8-15.2 |
| Cl ($\mu g\ g^{-1}$) | 9 | 705 | 106 | 547-901 | 8 | - | - | $<65$-176 |
| Br/Pb (w/w) | 7 | - | - | $<0.02$-0.12 | 7 | - | - | $<1.7$ |
| Cl/Br (w/w) | 9 | - | - | $>114$ | 8 | - | - | $<7.3$-$>43.9$[a] |

[a] = Cl or Br concentration $>$ detection limit only for two (different) samples

### 6.3.4 Other Sources

Apart from those already referred to, the only other potentially important source of Pb and $Br^-$ in catchment runoff appears to be dirt washed from the underside of vehicles by splash and spray during storm events. This dirt would be expected to contain a significant Pb and possibly Br content as it probably arises from exhaust products, engine oil, traffic fume, road dirt, etc. Quantification of this source is extremely difficult and has not been attempted in this work. It is noteworthy, however, that the VFDS (vehicle flow during sampling) parameter was not found to be significant in explaining the variations in runoff Pb loads analysed in section 5.6.3(b), which suggests that this source may not be significant.

In conclusion, therefore, the data presented concerning primary sources of Pb and $Br^-$ in the site area indicates with little ambiguity that vehicle emissions are the chief source of Pb and a major source of $Br^-$ and that de-icing salt is the second major source of $Br^-$ during the winter months.

## 6.4 Bromide, Lead and Chloride in Deposition and Road Surface Dust

In the absence of de-icing activities in the summer period, vehicle emissions have been shown to be the main source of $Br^-$ and Pb in the catchment. Deposition and road surface dust data from this period are therefore presented separately from the preceding source data, since they are considered to be steps in the pathway between Br and Pb in vehicle emissions and the presence of these elements in runoff, rather than primary sources.

### 6.4.1 Deposition

#### (a) Deposition Rates

General details concerning the five deposition sampling runs were given in section 5.3.1 and Appendix 4. In section 5.4, concerning background contributions to runoff quality, all concentration data obtained from the roadside gauges were treated on an equal basis for comparison with the farm gauge. In order to examine $Br^-$-Pb* and $Br^-$-$Cl^-$* relationships in deposition more fully, however, the $Br^-$, Pb and $Cl^-$ concentration data have been converted to deposition rates

(mg $m^{-2}day^{-1}$) in order to minimise the arbitrary effects of dilution in roadside gauges by varying amounts of relatively unpolluted background rainfall. These data have been summarised in Table 6.5 by treating all samples collected at the same distance from the hard shoulder on an equal basis and taking the arithmetic mean of the deposition rates found at those positions. An identical approach was taken to the data for the dry sampling run, but this data has been classified as dry deposition and is tabulated separately in Table 6.6. For total deposition data in Table 6.5, statistical comparisons between mean deposition rates at different distances from the hard shoulder are summarised in Table 6.7. As in section 5.5, the data from the farm gauges are regarded as representing background conditions.

TABLE 6.6 : Dry deposition data summary

| Distance from edge of hard shoulder (m) | Dry deposition rates (mg $m^{-2}day^{1}$) | | | Br/Pb | Cl/Br |
|---|---|---|---|---|---|
| | $Br^-$ | Pb | $Cl^-$ | (w/w) | (w/w) |
| 0.5 | 0.48[a] | 3.44[b] | 3.24[a] | 0.14 | 6.8 |
| 2.5 | 0.26[a] | 2.46[b] | 1.74[a] | 0.11 | 6.7 |
| 4.5 | 0.20[b] | 1.45[b] | 1.52[b] | 0.14 | 7.6 |
| ~600 | (0.002)[c] | <0.03[a] | (0.39)[c] | - | - |

[a] = one sample

[b] = mean of two samples

[c] = mean of June, July and August 1971 dry deposition data from Wraymires, Cumbria ( Cawse and Pierson, 1972).

* For clarity and uniformity, the symbols '$Br^-$' and '$Cl^-$' will be used in section 6.4.1 to refer to the bromide and chloride content of both wet and dry deposition, but 'Br/Pb' and 'Cl/Br' will be used to denote element ratios in all media throughout the remainder of section 6.

TABLE 6.5 : Total deposition data summary

| Distance from edge of hard shoulder (m) | Number of Samples | $Br^-$ Deposition Rate ($mg\ m^{-2}day^{-1}$) | $Br^-$ Deposition RSD (%) | Pb Deposition Rate ($mg\ m^{-2}day^{-1}$) | Pb Deposition RSD (%) | $Cl^-$ Deposition Rate ($mg\ m^{-2}day^{-1}$) | $Cl^-$ Deposition RSD (%) | Br/Pb (w/w) (RSD) | Cl/Br (w/w) (RSD) | Correlation Coefficients and Significance Levels* $Br^-$-Pb Rates | Correlation Coefficients and Significance Levels* $Cl^-$-Br Rates |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 6 | 0.52 | 27 | 3.00 | 35 | 7.15 | 28 | 0.18 (11) | 15.1 (53) | 0.973 (>0.99) | -0.467 (<0.9) |
| 2.5 | 8 | 0.30 | 20 | 1.60 | 22 | 5.01 | 39 | 0.20 (33) | 17.2 (46) | -0.461 (<0.9) | -0.088 (<0.9) |
| 4.5 | 8 | 0.20 | 14 | 0.98 | 44 | 3.80 | 62 | 0.23 (28) | 18.5 (52) | 0.832 (>0.98) | 0.525 (<0.9) |
| ~600 m | 4 | 0.02 | 17 | 0.03 | 35 | 1.68 | 33 | 0.80 (36) | 82.1 (23) | 0.224 (<0.9) | 0.767 (<0.9) |

RSD = Relative Standard Deviation
* in brackets

TABLE 6.7 : Statistical comparisons of some mean values from Table 6.5

| Distance Comparison (m) | t-test significance levels for differences between means | | | | |
|---|---|---|---|---|---|
| | Deposition Rates | | | Deposition rate ratios | |
| | $Br^-$ | Pb | $Cl^-$ | Br/Pb | Cl/Br |
| 0.5-4.5 | $\geq$0.99 | $\geq$0.99 | $\geq$0.98 | 0.9-0.95 | $\leq$0.9 |
| 4.5-600 | $\geq$0.99 | $\geq$0.99 | $\geq$0.95 | $\geq$0.95 | $\geq$0.99 |

(b) Total Deposition

Table 5.3 (section 5.4) showed that Pb and $Br^-$ total deposition concentrations in the roadside gauges were very much larger than in the farm gauge. As expected, this trend is equally noticeable in the deposition rates (Table 6.5), with $Br^-$ and Pb rates at the hard shoulder lying between one and two orders of magnitude greater than those at the farm gauge, and this again emphasises that the motorway was the main source of $Br^-$ and Pb in the site area. In contrast, the mean $Cl^-$ deposition rate at the roadside was only four times higher than background, and although this difference is statistically significant at $p \geq 0.95$ (Table 6.7), this trend again appears to reflect the presence of substantial background $Cl^-$ sources, as evident in the air sampling data. For all three elements, however, the difference in deposition rates between 0.5 m and 4.5 m is statistically significant at $p \geq 0.95$, and illustrates the considerable decline in rates within only a short distance from the carriageway, an effect also noted by Little and Wiffen (1978) in the case of Pb. The close association between $Br^-$ and Pb found in the air data is also evident in the correlations between $Br^-$ and Pb deposition rates (Table 6.5), although the reasons for the negative correlation at 2.5 m are not clear. Because of the small numbers involved ($n = 4$), the significance of relationships between background values cannot be realistically assessed.

The relative distribution of Pb, $Br^-$ and $Cl^-$ in the samples between filtrate and solid-associated fractions was found to be generally similar to that for runoff. In all samples, $Br^-$ and $Cl^-$ were found

predominantly in the filtrate, with the solid associated fraction ranging between < 1 and 20% of total sample mass for $Br^-$ and between < 0.4 and 12.5% for $Cl^-$, while for Pb the corresponding figures were 72 and > 99.8%.

(c) Dry Deposition Contribution

A tentative assessment of the relative contributions of wet and dry deposition to the total $Br^-$, Pb and $Cl^-$ deposited in the gauges can be gained from a comparison of the data in Table 6.5 with the dry deposition data in Table 6.6. Although the number of dry deposition samples was small, there was a noticeable similarity between total and dry rates for $Br^-$ and Pb at the roadside gauges, which suggests that dry deposition was the major mode of deposition of these elements in the gauges.

Additional evidence of this for Pb comes from the study of Pb dry deposition to soil and grass besides the M4 motorway by Little and Wiffen (1978). For comparison, relevant data from their work (after adjustment for differences in vehicle flow and lower petrol Pb content in the present work) are presented along with Pb total and dry deposition data in Table 6.8. It can be seen therein that the general range of Pb dry deposition rates found by them is very similar to both dry and total rates from the present work, and this strengthens the case for concluding that most Pb found in the gauges in the present work arose from dry deposition.

TABLE 6.8 : Comparisons of Pb deposition data with published work

| Author | Distance from edge of hard shoulder (m) | Pb deposition rates ($mgm^{-2}day^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Total | | Dry | |
| | | Mean | Range | Mean | Range |
| This work | 0.5 | 3.00 | 1.63-4.38 | 3.44[a] | 2.51-4.36 |
| | 4.5 | 0.98 | 0.49-1.83 | 1.45[a] | 1.41-1.49 |
| Little & Wiffen (1978) | 0.0 | - | - | 2.01 | 1.18-3.67 |
| | 5.0 | - | - | 0.79 | 0.41-1.22 |

[a] = mean of two samples

Because of the close associations between Pb and Br in air and deposition already noted, it is almost certain that dry deposition would have been the major mode of $Br^-$ deposition in the gauges. The dominant contribution of this mode to deposition of both elements is a reasonable conclusion, since traffic flows were generally high and prolonged (typical southbound weekday 24 h range 280-3300 vehicles $h^{-1}$) leading to Pb and Br emission on a relatively continuous basis, whereas the background Pb and $Br^-$ content of rain was very low (Table 5.3). Although some washing-out of the highway aerosol would probably have occurred during rain itself, part of this would have been deposited as dry deposition anyway if no rain had occurred.

In contrast to the trends noted for $Br^-$ and Pb, deposition rates for $Cl^-$ show that dry rates are in the region of half those for total deposition in all the roadside gauges, and suggests that rainfall $Cl^-$ content contributes a significantly greater share to overall $Cl^-$ deposition than for Pb or $Br^-$. A similar trend in $Cl^-$ deposition data from other sites in the UK was noted by Cawse (1981).

Far fewer comparative data are available in the literature for $Br^-$ and $Cl^-$ deposition at motorway locations than for Pb, and Mance (1982) reported that only one of seven UK studies of stormwater quality had included data on aerial deposition rates of the pollutants studied, that of Mance and Harman (1978). In that work, no $Br^-$ data was given, but an average $Cl^-$ deposition rate of 14.6 mg $m^{-2}day^{-1}$ (measured over two years) was reported for a gauge in the Stevenage New Town area. This is in reasonable agreement with the roadside rates found in this work, considering that $Br^-$ and $Cl^-$ deposition rates can increase considerably in winter due to changes in meteorological conditions (Cawse and Pierson, 1972). Thus a mean daily figure based on year-round data will often have a higher value than a value based on summer-only data, as in this work. Background rates (600 m) for $Br^-$ and $Cl^-$ found here are also in reasonable agreement with values given by Cawse (1981) when similar differences in sampling period are taken into account.

(d) Element Ratios

Table 6.5 shows that the mean ratio of $Br^-$ and Pb total deposition rates at the roadside lies in the range 0.18-0.23. This is about half the mean value found for air samples (0.49), and the difference indicates clearly that a process of Br loss from Pb exhaust particulates has taken place between emission, deposition and washing of the gauges by rainfall. As noted in section 1.2.2(a), loss of Br from exhaust-derived particulates in ambient air has been widely (although not universally) observed, but in the present case a loss mechanism appears to be operating with deposition samples but not with air particulates.

One possible explanation may be derived from the discussion of the air data in section 6.3.2, where it was noted that the particulates trapped on the filter had probably lost little or no Br between emission and deposition, and that some trapping of $NH_4Br$ (from exhaust) or HBr (from halide loss after deposition) may also have occurred. This would not have been the case with fresh particulate deposited in the gauges, since any Br lost in gaseous form would have been rapidly dispersed into the surrounding air. Following the first rainfall, however, any further Br loss from previously deposited particulate matter would have been immediately solubilised and remained within the body of collected water. It may be because this loss restricting mechanism would not have operated with dry deposition that the Br/Pb ratios found in those samples (Table 6.6) were generally lower than those in total deposition. Once rainfall was over, however, Br loss to atmosphere from any particulates subsequently deposited and retained on the dry gauge funnel itself would continue. Thus, although the filter data precludes loss of Br between emission and deposition on the filter, different considerations would have applied to material deposited in the gauges during dry weather.

Another important possible reason for low Br/Pb ratios which must be considered is the redistribution of very Br-deficient road surface dust (with a high Pb content) over the gauges by vehicle generated turbulence and prevailing winds. Table 6.9 shows that the prevailing Br/Pb ratios in this dust were very low. These data are discussed in more detail in section 6.4.2 following, but it was clear

from the appearance of the solids found in the gauges that a significant fraction consisted of road surface dust and soil from the verge. The processes of Br loss, deposition and particle agglomeration and possible Br leaching which appeared to affect particulates between emission and dust accumulation on the road surface have not been fully documented in the literature, but from the dust data it is clear that a reservoir of Br-deficient material was present on the carriageway and hard shoulder (and no doubt the verge) which would have significantly lowered the deposition Br/Pb ratio if re-suspended and deposited in the gauges, even if all freshly deposited material had Br/Pb values of ~0.49 and lost no Br after deposition. Comparison of the general range of road dust, deposition and air particulate ratios suggest that, if little Br was lost from freshly deposited particulates, the contribution of re-suspended road surface dust to deposition Pb loads is approximately half of the total. The small but statistically significant increase in the Br/Pb ratios in total deposition at 0.5 and 4.5 m (0.18 and 0.23 respectively, Table 6.5) may point to a slight lessening of the deposition of Br-deficient dust at the 4.5 m gauge. In conclusion, however, it is clear that both of the possible causes advanced to explain the difference between air and deposition Br/Pb ratios (i.e. volatile loss or incursion of dust into the gauges) may have played a role in producing this effect.

The main feature of the total deposition Cl/Br ratios (Table 6.5) is the large increase between the roadside range (15.1-18.5) and the background value of 82.1. The background value is comparable with those given by Cawse (1981) for rural sites in the UK, so the noticeable decrease in roadside gauges is very probably additional evidence that the motorway is the main source of Br in the area. The background Br/Pb ratio, 0.8, is again comparable to rural values determined by Cawse (1981) and almost certainly reflects the predominance of a background contribution to the much lower deposition rates found at this gauge than at the roadside.

### 6.4.2 Road Surface Dust

Lead data for two road dust samples batches were presented in Fig. 5.24 (samples '1' and '2'). The subsamples from sample 2 were also analysed for their Br and Cl content using INAA (section

3.9.2(d)) in conjunction with five other subsamples from an additional sample batch, giving 17 subsamples in total. The resultant Pb, Br and Cl data are summarised in Table 6.9.

TABLE 6.9 : Road dust samples data summary

| Element Concentration or Ratio | Mean[a] | RSD(%) | Range |
|---|---|---|---|
| Br ($\mu g\ g^{-1}$) | - | - | <25 - 167 |
| Pb ($\mu g\ g^{-1}$) | 3156 | 45.3 | 2185 - 7090 |
| Cl ($\mu g\ g^{-1}$) | - | - | <121 - 908 |
| Br/Pb (w/w) | - | - | <0.004-0.063 |
| Cl/Br (w/w) | - | - | <2 - >27.5 |

[a] = number of samples is 17
RSD = Relative standard deviation

As noted in section 5.5.5(b), the Pb concentrations are comparable to those found in similar locations by other workers (e.g. Harrison, 1979; Ellis and Revitt, 1982). The INAA analysis of Br and Cl utilised the the short irradiation/ decay scheme as described (sections 3.9.1(a). Under these conditions, the samples displayed high background activity during counting which led to higher detection limits (especially for Cl) than with some other types of sample, as evident in Table 6.9. Nonetheless, Br concentrations compare favourably with the limited amount of published data available for Br in street and road dusts, notably that given by Farmer and Cross (1978) and Hopke et al. (1980), although these authors gave no Cl data for their samples. In the present samples, unlike Pb, there was no relationship between Br concentrations and particle size, and the main significance of the data is the striking difference between Br and Pb concentrations, which is such that Br/Pb ratios are much lower than those in the air and deposition data previously discussed. This result agrees well with the very marked tendency for the majority of $Br^-$ in runoff and total deposition to be found in the filtrable frac-

tion, as noted previously (sections 6.2 and 6.4.1(b)). Taking this effect together with Br/Pb ratios in air and deposition, it is clear that Br is lost from Pb particulates by a combination of volatilisation and leaching processes. As noted in section 1.2.2(a), although the loss of Br from ambient Pb aerosol has been widely investigated, the decomposition of PbBrCl in a polluted aqueous environment (such as road runoff) is far less well documented. Such evidence as exists, however, clearly supports the existence of the Br leaching effect found in this work, and confirms the dominant tendency of Pb to remain solid-associated. This process would suggest that Br is more easily removed in runoff from a road surface than Pb.

## 6.5 Bromide Loads in Runoff

### 6.5.1 Factors Affecting Bromide Loads

In Section 5.6, the effects of a range of environmental variables (given in Table 5.10) on TSS, Pb, Zn and $Cl^-$ loads were examined using linear regression analysis. Interrelationships between parameters were also examined where appropriate. A similar approach has been adopted to examine the main factors affecting $Br^-$ loads. Data for 21 events were available, nine from winter and twelve from summer. Individual event loads are given in Appendix 5. Partially sampled events (W5, 6, 13 and S5 and 11) were excluded from correlations with ADPT for reasons given in section 5.6.3(c), and the Pb load value for event S8 has been excluded from all Pb data examined in this section for reasons explained in section 5.6.3(b).

The most important results of the correlations are given in Table 6.10, where it should be noted that correlations have been carried out on winter and summer data separately as well as combined, in order to emphasize seasonal differences in relationships. With all correlations involving winter $Br^-$ loads, it was recognised that the influence of $Br^-$ in de-icing salt could arbitrarily affect the degree of correlation with Pb and $Cl^-$. In order to minimise this as far as possible, these correlations were repeated using $Br^-$ winter load data adjusted for salting effects, and the results are also presented in Table 6.10 (part B) for comparison. The adjusted load data used are identical to those used to derive adjusted FWM values in Table 6.1 (section 6.2.2) and are given in Appendix 5. Summer load correlations are included in both part A and B to facilitate comparisons.

TABLE 6.10 : Correlations between $Br^-$, Pb and $Cl^-$ loads in runoff

| Correlation | No. of Events | PART A | | PART B (Winter Br loads adjusted for salting) | |
|---|---|---|---|---|---|
| | | Correlation Coefficient | P Value of Coefficient | Correlation Coefficient | P Value of Coefficient |
| BrL-ClL | 21 (w+s) | 0.868 | >0.99 | 0.541 | >0.98 |
| | 9 (w) | 0.910 | >0.99 | 0.653 | 0.9-0.95 |
| | 12 (s) | 0.947 | >0.99 | 0.947 | >0.99 |
| BrL-PbL | 15 (w+s) | -0.018 | <0.9 | 0.111 | <0.9 |
| | 8 (w) | 0.316 | <0.9 | 0.622 | 0.9-0.95 |
| | 7 (s) | -0.397 | <0.9 | -0.397 | <0.9 |
| BrL-ADPT | 16 (w+s) | 0.442 | 0.9-0.95 | 0.422 | <0.9 |
| | 6 (w) | 0.388 | <0.9 | 0.095 | <0.9 |
| | 10 (s) | 0.676 | >0.95 | 0.676 | >0.95 |

BrL = bromide load
ClL = chloride load
s = summer events
w = winter events

As noted in section 6.2, $Br^-$ in runoff was found to be almost entirely in soluble form, while de-icing salt was also observed to contribute significantly to winter $Br^-$ concentrations. In addition, the Br/Pb ratios in deposition and road dust compared with that in air were found to clearly indicate loss of Br from Pb particulates by volatilisation or leaching processes or both. In view of these trends, it is not surprising that Table 6.10 (part A) shows strong association between $Br^-$ and $Cl^-$ loads in all three correlations, while those with Pb loads are all much weaker. Bromide loads also show a tendency to be correlated with ADPT, and this was most strongly marked in summer events when the influence of de-icing salt was absent, as also found in the case of Cl (section 5.6.3(c)). No other environmental variables, notably VFDS, gave significant direct correlations with $Br^-$ loads.

Part B of Table 6.10 shows the effects of removal of the de-icing salt component from winter $Br^-$ loads. Significantly, correlations with $Cl^-$ loads are noticeably weakened, and, recalling that $Cl^-$ winter loads are largely dominated by salting effects, this underlines the fact that adjusted $Br^-$ loads are derived largely from a different source i.e. vehicle emissions, and therefore are not so strongly linked to Cl loads in winter following adjustment. Correlations with Pb loads and ADPT involving adjusted $Br^-$ loads show no distinctive trend compared with part A; the increased coefficient for the winter-only BrL-PbL correlation, 0.622, may have reflected the removal of a de-icing salt effect, but nonetheless the coefficient only just achieved significance at $p > 0.9$. Overall, therefore, in comparison with the relationships found between Br, Pb and Cl in air and deposition, the table clearly shows a markedly stronger relationship between $Br^-$ and $Cl^-$ in runoff, while the previously strong relationships between Br and Pb are much less noticeable. These trends therefore strongly suggest a clear breakdown in runoff of the previously close associations between Br and Pb. An example of this in an individual event is clear from Fig. 6.4.

### 6.5.2 Bromide/Lead (Br/Pb) Ratios in Runoff

The dissociation between $Br^-$ and Pb in runoff is especially apparent when runoff Br/Pb ratios are considered. For each event which

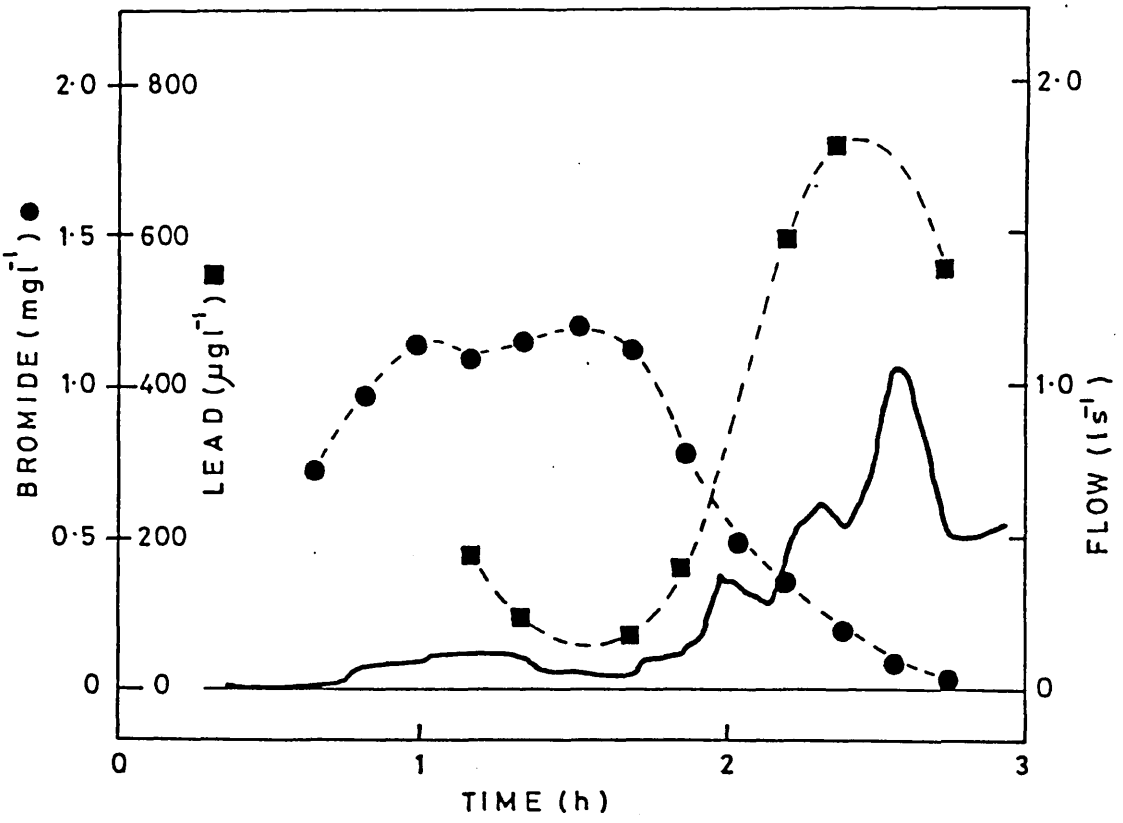



Figure 6.4 Typical hydrograph showing in-storm dissociation between $Br^-$ and Pb

was analysed for both parameters, the ratio $Br^-$load/Pb load was calculated, using adjusted $Br^-$load data as before in order to minimise the effects of salting. These values are presented according to their corresponding event numbers in Fig. 6.5, together with air and deposition mean Br/Pb values for comparison.

The figure illustrates the striking contrast between the variability in runoff Br/Pb values and the relatively narrow range evident in air and deposition. In order to clarify the source of this variability, correlations between Br/Pb values and $Br^-$ and Pb load values were carried out, and the results are given in Table 6.11. It is clear from the table that variation in Pb loads has a much greater effect on changes in Br/Pb values than variation in $Br^-$ loads, and correlations between logged values of these data (Table 6.11) emphasize the difference still further. Lead load data (Appendix 5) indicates clearly that Pb loads showed greater variability than those of $Br^-$(adjusted), even when the partial sampling of some events is taken into account. Excluding those events (W5, 6, 13 and S5 and 11), the mean and RSD of all remaining Pb loads are 1.94 g and 97% respectively, while the corresponding figures for $Br^-$are 1.30 g and 61%. In view of the dissociation between $Br^-$ and Pb in runoff previously demonstrated, it appears that the contrasting variation in Pb and $Br^-$ loads is closely linked with the different mechanisms affecting their accumulation on and removal from the catchment, which were evident in the results of the regression analyses of Pb and $Br^-$load behaviour previously presented (sections 5.6.3(b) and 6.5.1 respectively). These showed that $Br^-$and Pb (and hence Br/Pb ratios) would have been affected by at least two virtually independent environmental variables: storm (and hence runoff) characteristics in the case of Pb loads, ADPT in the case of $Br^-$loads. (In the case of $Br^-$, these mechanisms appear to have led to less relative variation in loads than with Pb). In contrast, because of their physical state and closer association in air and deposition, the Br and Pb content of these samples could not have varied independently to nearly the same extent as in runoff. In consequence, therefore, runoff Br/Pb ratios would have been expected to show much greater variation than in air and deposition, and Fig. 6.5 demonstrates quite clearly that this was indeed the case.

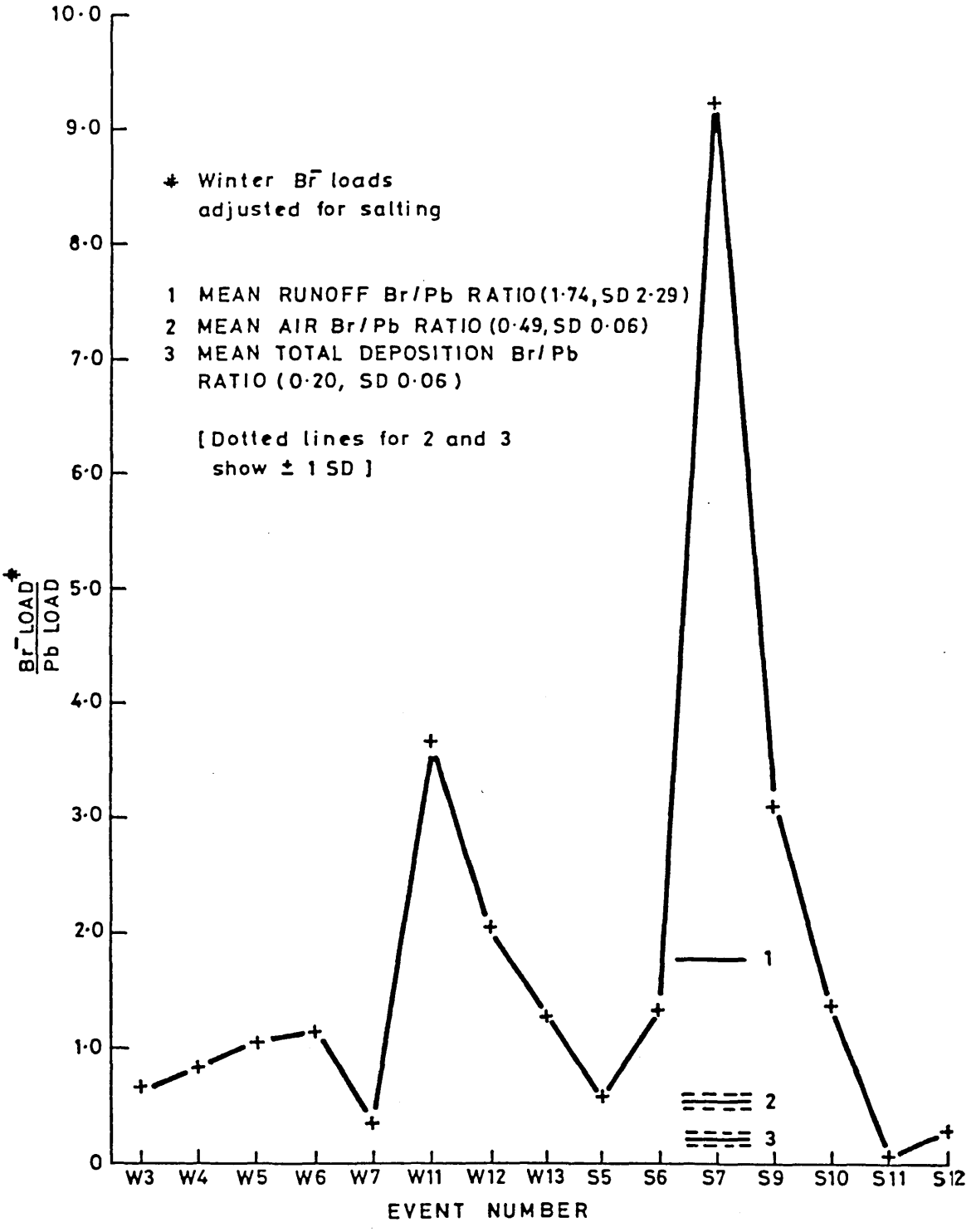



Figure 6.5 Relationship between Br/Pb ratios in runoff, air and deposition

TABLE 6.11 : Correlations between Br/Pb ratios in runoff and $Br^-$ and Pb loads

| Correlation * | Correlation coefficient | Percentage fit | P value of coefficient |
|---|---|---|---|
| ABrL/PbL-ABrL | -0.003 | $<0.1$ | $<0.9$ |
| ABrL/PbL-PbL | -0.481 | 23.2 | 0.9-0.95 |
| $\log_{10}$(ABrL/PbL)-$\log_{10}$ABrL | -0.144 | 2.1 | $<0.9$ |
| $\log_{10}$(ABrL/PbL)-$\log_{10}$PbL | -0.807 | 65.1 | $>0.99$ |

* refers to 15 events in all cases (8 winter, 7summer)
ABrL = winter Br loads adjusted for salting together with summer loads
PbL = Pb loads

Figure 6.5 also illustrates a clear tendency for runoff Br/Pb ratios to be significantly higher than the ambient air ratio, 0.49, which is in considerable contrast to both deposition and road dust data (Tables 6.5 and 6.9) The mean ratio for 15 events (using adjusted winter $Br^-$ loads) was 1.79, RSD 128%. Although the range was wide, the difference between this value and that for air is still statistically significant at $P > 0.95$. A more precise way of assessing the relative amounts of $Br^-$ and Pb in runoff for the events sampled, however, is to calculate the ratio $\Sigma Br^-$ load/$\Sigma$Pb load for all events analysed for both $Br^-$ and Pb (n = 15); this gives a value of 0.62. If the deposition and dust ratios previously discussed (section 6.4) were typical of the relationship between the average long term levels of $Br^-$ and Pb on the carriageway, this high ratio appears to indicate that proportionately more $Br^-$ than Pb was removed during runoff events, especially if road dust, with its very low Br/Pb ratios (Table 6.9) was a major reservoir of $Br^-$ on the catchment. This apparent tendency for $Br^-$ to be removed more easily than Pb from the catchment would be in accordance with its essentially soluble form in runoff (as previously noted) and the "first flush" behaviour during individual events, as evident in Fig. 6.2. Removal would therefore have taken place under both low and high flow conditions, while Pb removal, being predominantly associated with solids movement and therefore related to

volumes and flow rates, would have been more restricted during low flow conditions.

### 6.5.3 Bromide Accumulation in the Catchment

In section 6.5.1, it was noted that the main environmental variable correlating directly with $Br^-$ loads was ADPT, which suggests that $^*Br^-$ accumulated in some way within catchment A during dry periods. It was apparent from Table 6.10 that the relationship with ADPT during the winter period was masked to some extent by the influence of de-icing salt. In order to eliminate this problem, therefore, the more detailed examination of accumulation of $Br^-$ in the catchment which follows will be confined to summer events only, excluding S5 and S11 as before. Since the ultimate intention of this section is to relate $Br^-$ runoff loads and $Br^-$ deposition rate data (Section 6.4) which are given in time-based units (mg $m^{-2}day^{-1}$), $Br^-$ accumulation will be analysed in terms of antecedent dry period (ADP) rather than ADPT. This is legitimate since ADP and ADPT are very closely correlated ($r = 0.998$) and ADP = 0 when ADPT = 0.

Figure 6.6 illustrates the variation of runoff $Br^-$ loads with ADP. Although there is considerable scatter in the data, a trend towards a limiting value of $Br^-$ loads with increasing ADP is clearly discernible. Significantly, a very similar pattern is evident in the summer $Cl^-$ load data (Fig. 6.7), and this type of trend in the variation of pollutant loadings on road surfaces with time has been observed by other workers in the field, notably Sartor and Boyd (1972) and Pitt (1979), who noted that pollutant accumulation rates tended to be highest during the first few days following a rainfall or street cleaning event. Rates then decreased and eventually approached zero, and this was explained by resuspension and removal by wind and traffic-related turbulence. The maximum accumulated load was reached when deposition and removal rates became equal. This process can be represented mathematically (Shaheen, 1975; Alley and Smith, 1981) by the equation

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* For consistency with its use in section 6.4.1 concerning deposition data, '$Br^-$' will be used in this section when referring in the text to the bromide/bromine load accumulated during dry periods.

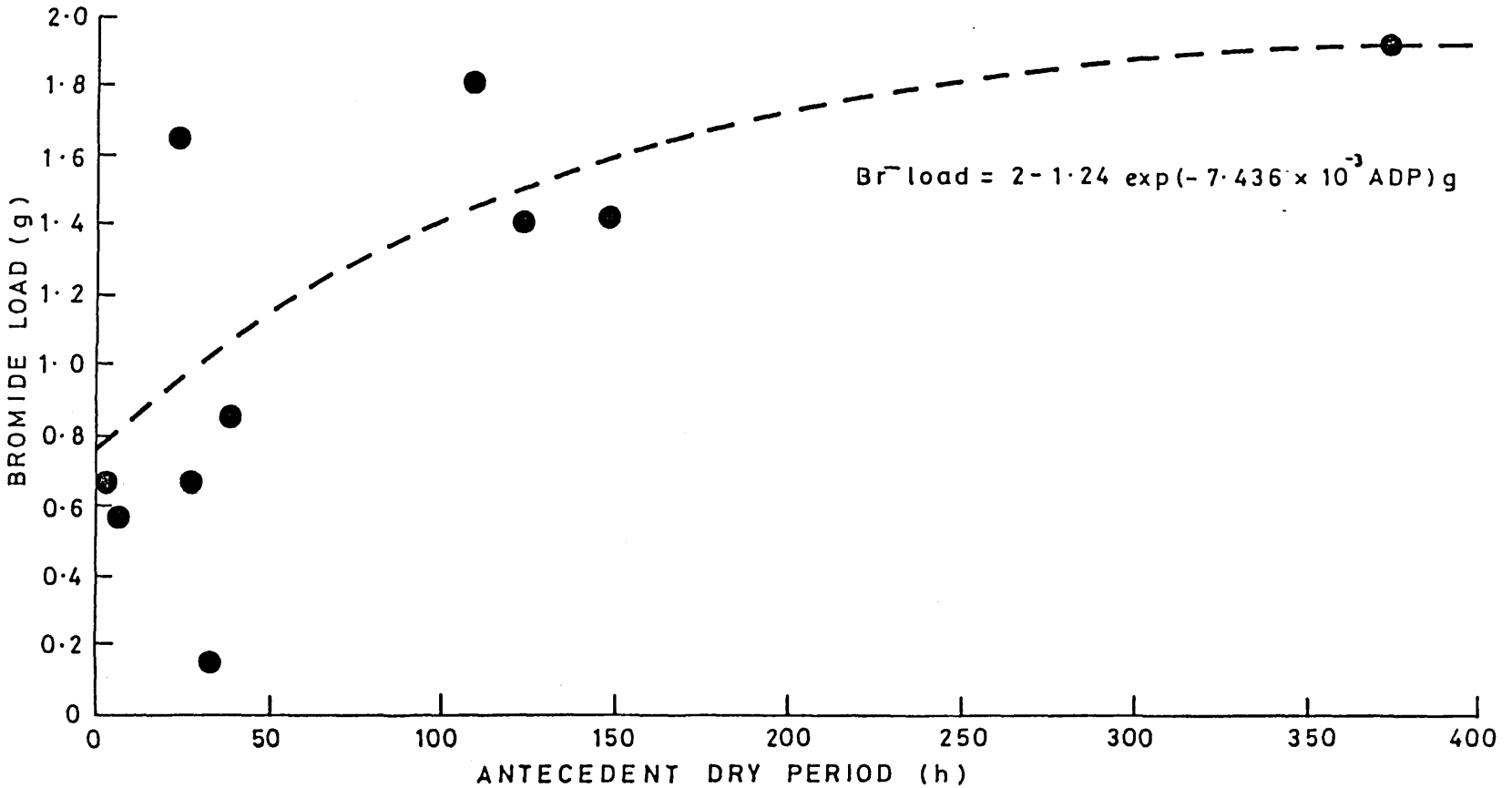



Figure 6.6 Relationship between runoff $Br^-$ loads and ADP

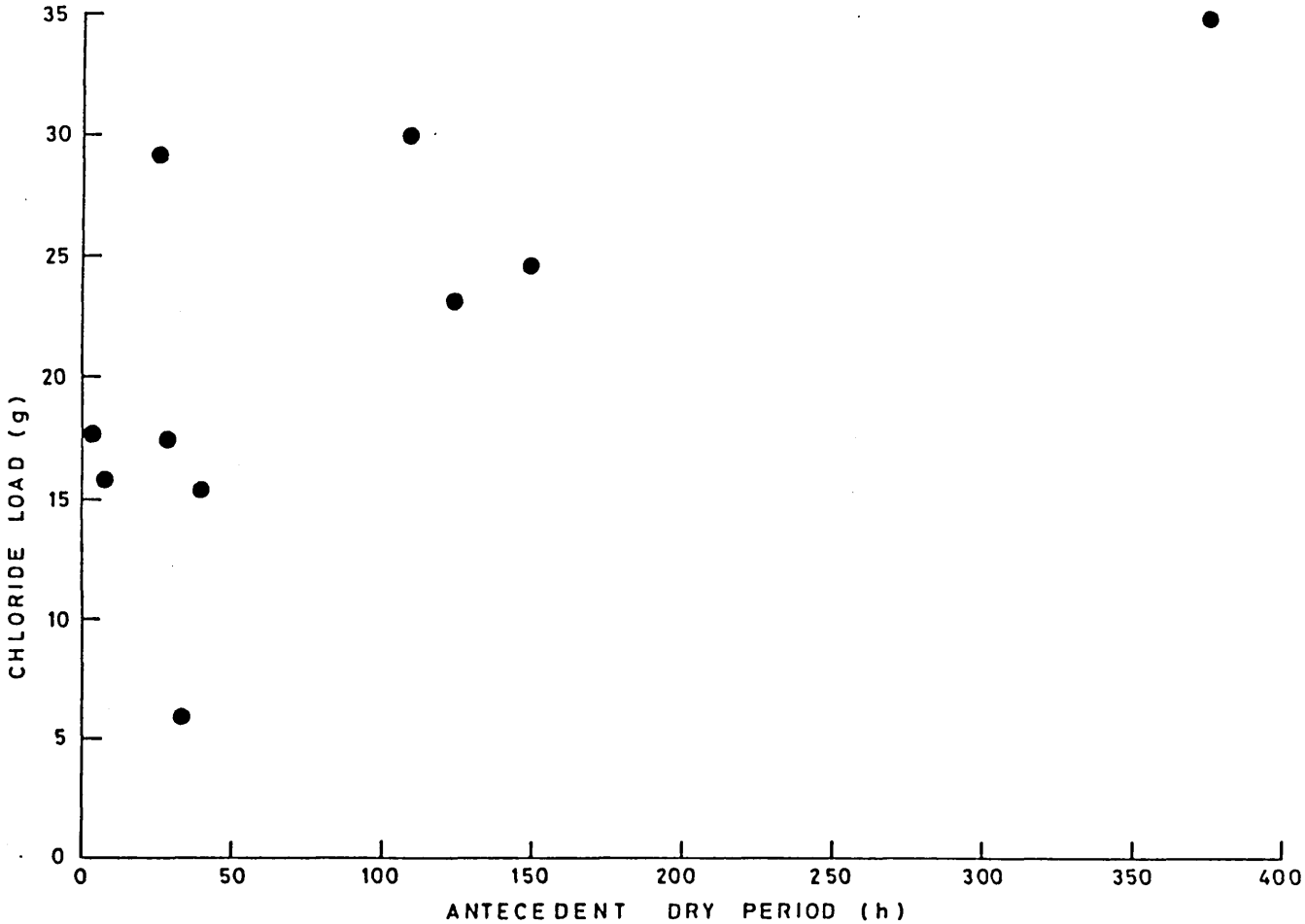



Figure 6.7 Relationship between runoff $Cl^-$ loads and ADP

$$\frac{dL}{dT} = K - K_2 L \qquad (1)$$

where $L$ = amount of pollutant per unit area ($g\ m^{-2}$)

$K$ = constant rate of pollutant deposition ($g\ m^{-2}h^{-1}$), assuming this is mainly derived from a steady traffic flow.

$K_2$ = rate constant for constituent removal ($h^{-1}$)

$T$ = time (h)

In addition to removal by wind or turbulence, $K_2$ can also account for pollutant removal by e.g. chemical degradation, or other processes, depending on the material of interest. Integration of (1) leads to

$$L = L_{max}(1 - \exp(-K_2 T)) \qquad (2)$$

where $L_{max}$ = the maximum loading which can normally accumulate, i.e. when deposition rate = removal rate

This curve is shown in Fig. 6.8 (curve A), from which it is clear that use of equation (2) to model pollutant accumulation would require the assumption that the pollutant concerned was completely removed by the last runoff (or sweeping) event i.e. when $T = 0$, $L = 0$. To eliminate this assumption, Alley and Smith (1981) proposed the use of an "equivalent accumulation time", defined as

$$T = t + t_e \qquad (3)$$

where $t$ = time since last runoff or sweeping event (h)

$t_e$ = time required (h) for surface load equal to that present at the <u>end</u> of the last runoff/sweeping event to accumulate (this load is $L_e$ in Fig. 6.8)

Figure 6.8 illustrates the relationship between a curve incorporating $t_e$ (curve B) and one without (curve A).

Although the situations represented in Fig. 6.8 refer to pollu-

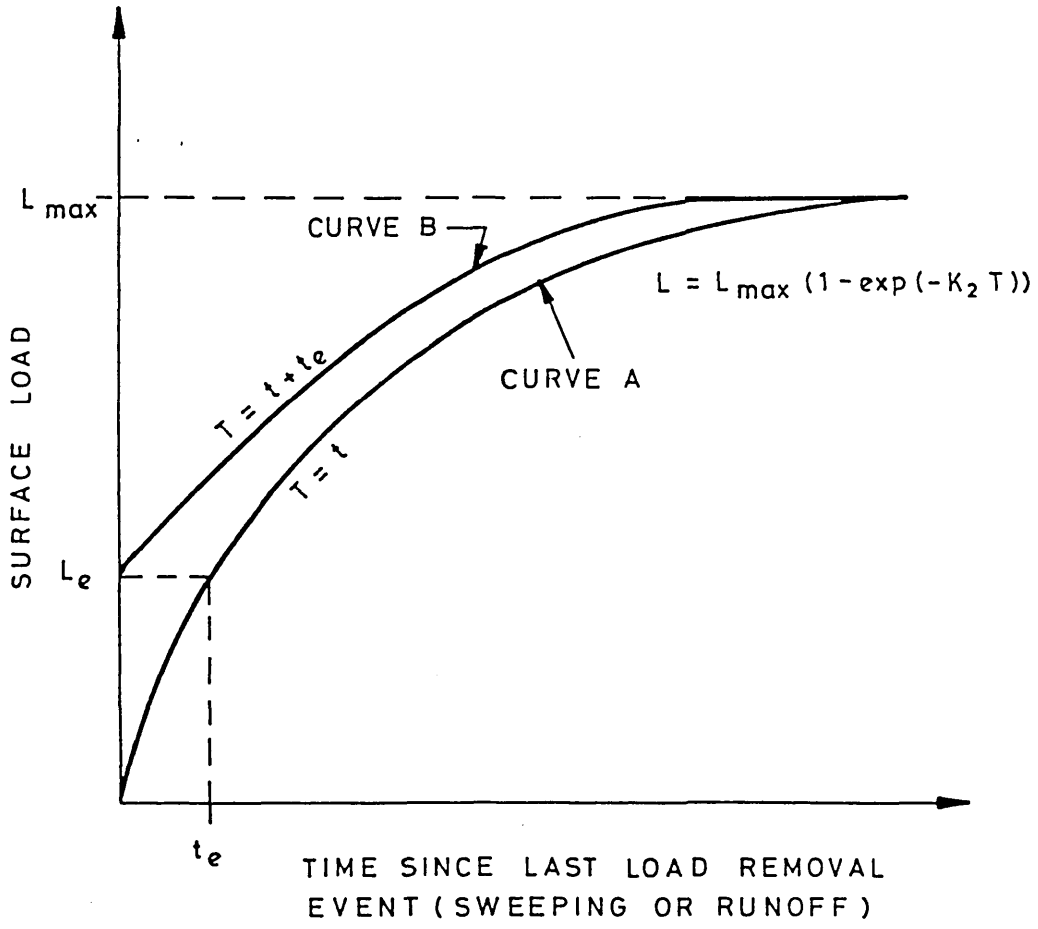



Figure 6.8 Model pollutant accumulation curves (after Alley and Smith, 1981)

tant accumulation during a single dry period following a preceding removal event, Fig. 6.6 is analagous to these curves if it is considered that each $Br^-$ load removed in a runoff event is reasonably representative of the $Br^-$ load accumulated on the catchment at the beginning of the event. Then each runoff load is effectively equivalent to a point on a $Br^-$ accumulation curve. On this basis, the relationship between $Br^-$ runoff loads and ADP in the present work can be modelled in a similar manner to pollutant accumulation by an equation of the form

$$BrL = L_m[1-\exp(-K_B\{t+c\})] \quad (4)$$

where $t$ = antecedent dry period (h)

$BrL$ = bromide load accumulated on catchment A at time t and subsequently in a runoff event (g)

$L_m$ = maximum surface loading on catchment A (g)

$K_B$ = a rate constant ($h^{-1}$)

$c$ = a constant, analagous to $t_e$ in equation (3), which is included initially to cater for any residual load which might exist at t = 0

Equation (4) can also be expressed as

$$BrD = L_m\exp(-K_B\{t+c\}) \quad (5)$$

where $BrD$ = the "bromide deficit" (= $L_m$ - BrL), which is the difference between the limiting load and the load already accumulated at time t

Differentiation of (5) with respect to t gives

$$dBrD/dt = -L_mK_B\exp(-K_B\{t+c\}) \quad (6)$$

When t = 0,

$$dBrD/dt = -L_mK_B\exp(-K_Bc) \quad (7)$$

and, if c is small or zero,

$$dBrD/dt = -L_mK_B \quad (8)$$

Equation (8) is thus an expression, in units of time, for the initial rate of deficit decrease and is therefore numerically equal to the rate of load increase (or $Br^-$ deposition rate) at t = 0. By use of suitable units, this allows direct comparison with $Br^-$ deposition

values derived from deposition gauge data. This permits the possibility of directly linking $Br^-$ data from two entirely different sample types (runoff and deposition) and thus potentially clarifying some aspects of Br (and Pb) behaviour in the catchment.

The following procedure was adopted to achieve this:

Taking natural logarithms of both sides of equation (5) gives

$$\log_e BrD = \log_e L_m - K_B\{t+c\} \quad (9)$$

Writing $\log_e L_m - K_B c$ as a new constant, F, gives

$$\log_e BrD = F - K_B t \quad (10)$$

Thus a linear regression of $\log_e BrD$ on t will give an estimate for $K_B$. Since BrD = $L_m$-BrL, however, use of this approach requires the prior assumption of a value of the limiting load, $L_m$. In the light of the data in Fig. 6.6, a value of 2 g (over the entire area of catchment A) was considered reasonable. Thus

$$BrD = (2-BrL)g \quad (11)$$

A regression of $\log_e BrD$ against t led to the equation

$$\log_e BrD = 0.215 - 7.436 \times 10^{-3} t \quad (12)$$

for which r = -0.828 ($P > 0.99$) and $r^2$ = 68.5%. Since BrD = (2-BrL)g, the exponential form of equation (12) can also be written as

$$BrL = 2 - 1.24\exp(-7.436 \times 10^{-3} t) \quad (13)$$

and the line of this is shown in Fig. 6.6.

Comparing equation (12) with equation (10), it is clear that

$$K_B = -7.436 \times 10^{-3} h^{-1}$$

This value is statistically significant at $P > 0.99$. Use of this value in equation (8) in conjunction with the estimated value of 2 g for $L_m$ in order to estimate an initial $Br^-$ deposition rate from runoff data first requires an assessment of the magnitude of the term

$\exp(-K_B c)$ in equation (7). Since the intercept value of 0.215 in equation (12) is equivalent to $F(= \log_e L_m - K_B c)$, and $\log_e L_m = \log_e 2$, the size of the $-K_B c$ term is best assessed by comparing the 95% confidence limits of F (-0.350 to +0.789) with the value of $\log_e 2$, 0.693. From this it is clear that $\log_e 2$ falls within these limits, and thus on this basis the term $-K_B c$ will be considered negligible for the purposes of using equations (7) and (8).

In view of the significance of $K_B$, therefore, it was considered justifiable to produce a tentative estimate of the $Br^-$deposition rate from the product of $K_B$ and $L_m$ based on equation (8), assuming $L_m = 2$. This gives a value of $14.9 \times 10^{-3} gh^{-1}$ over the entire area of catchment A, or 0.45 mg $m^{-2}day^{-1}$. In view of the approximations involved, this is in excellent agreement with the range of mean deposition rates (total and dry) found from the gauge data at the roadside, 0.2 to 0.52 mg $m^{-2}day^{-1}$ (Tables 6.5 and 6.6), and suggests that the first order approximation for $Br^-$accumulation used to derive the runoff-based deposition rate is reasonably realistic.

It is also possible using equation (13) to estimate the time taken for the limiting value to be approached. In theory of course this will be infinite, but for practical purposes this may be taken as 90% of the limiting value. Rewriting equation (13) and substituting 'ADP' for 't' gives

$$ADP = (-1/7.436 \times 10^{-3}) \log_e([2-BrL]/1.24) \qquad (11)$$

When BrL = 1.8 g (i.e. 90% of 2 g, the estimated limiting value) ADP = 245 h or ~10 days, which is in reasonable agreement with the data in Fig. 6.6 and with Sartor and Boyd's data for pollutant accumulation on road surfaces (1972).

It was noted in section 6.4.1 that the bulk of $Br^-$and Pb found in the deposition gauges was very probably deposited in the form of dry deposition. In view of the comparability of the $Br^-$deposition rates derived directly from gauges and from runoff data, it is possible to estimate an approximate value for the Pb limiting load by dividing the estimated $Br^-$limiting value of 2 g by a suitable value of the Br/Pb ratio. For this purpose, the average dry deposition ratio of 0.13 (Table 6.6) seems most appropriate, which leads to a limiting

Pb load value of 2/0.13 or 15.4 g. Comparison of this value with the range of Pb runoff load values in Appendix 5 shows that this is a reasonable figure; the range of summer values was 0.09 to 8.0 g.

Inspection of the range of Br/Pb ratios found in road dust (<0.004 - 0.063, Table 6.9) shows that, had a figure in that range been used to derive the Pb limiting load, this would have led to a much higher value. Derivation of a Pb deposition rate from the $Br^-$ runoff data using a dust Br/Pb ratio would also have led to considerably higher value than found from deposition gauge data, if it were assumed that $Br^-$ and Pb loads reached their limiting values at the same time. There is no a priori reason, however, for $Br^-$ on the catchment to be entirely or even predominantly associated with the type of dust which was sampled on the hard shoulder and which gave rise to the data in Table 6.9. Although detailed investigation of the precise nature of the $Br^-$ "sink" on the catchment was beyond the scope of the present work, it appears reasonable to suggest that, even though Br was lost from Pb particulates by volatilisation, some of the Br so lost could subsequently have been adsorbed on the road surface itself quite independently of Pb movement. In view of the shift towards higher pH values in runoff samples from the general range found in total deposition, as noted in section 5.5.1, it is probable that the road surface itself was essentially basic or neutral in character (Harrison and Wilson, 1985a). This would therefore presumably have tended to adsorb acidic species (such as HBr) should these have been present in the air above the carriageway. The observed trend to a limiting value, were such an adsorption mechanism operative, may therefore have been due to either a gradual saturation of suitable adsorption sites with time, or possibly the establishment of an "equilibrium" position where adsorption became balanced by desorption and re-volatilisation.

Bromide adsorbed on the carriageway surface in this way would probably not have been affected during the sampling of loose road dust, and thus road dust Br/Pb ratios may not be representative of the Br/Pb ratio on the carriageway as a whole, as the runoff data suggest. Moreover, such surface-adsorbed $Br^-$, if present, may well have been concentrated on the surface of the travelling lanes rather than the hard shoulder. A similar possibility for oil and PAH was suggested by the data for these parameters presented and discussed in section

5.5.9. It also appears probable that a surface film of this kind would be readily removed during runoff, giving rise to the "first flush" effect evident in Fig. 6.2, whereas leaching of Br from dust similar to those samples analysed (if typical) would appear not to be a major source of readily available $Br^-$ because of the generally very low Br content. In the wider context of the impact of road runoff on receiving waters, however, and consideration of possible treatment methods to alleviate that impact, the most important aspects of $Br^-$ and Pb in runoff are undoubtedly the soluble nature of $Br^-$ and the solid associated nature of Pb.

# SECTION 7. MOTORWAY RUNOFF TREATMENT

## 7.1 Introduction

In the overview of the advantages of the M1 site given in section 2.1.3, it was emphasised that, as well as facilitating the study of the major variables affecting untreated runoff (UTR), the great similarity of the four catchments and their contiguous nature made them ideally suited for comparative studies of the treatment systems installed. Accordingly, the opportunity was taken during the present work to carry out a preliminary assessment of the effectiveness of the french drain (FD) and sedimentation tank (ST) in treating UTR. Effluents from these installations have been compared with UTR in two ways:

(a) On the basis of simultaneous bulk sampling of suspended solids at UTR and FD or ST drains, using the apparatus described in sections 2.4.1(b) and 2.4.2(b).

(b) On a wider basis with TSS, Pb, Zn and $Cl^-$ UTR event data (from section 5.5) in conjunction with ST and FD event data arising from the same sampling period.

All these comparisons are made by considering untreated runoff as the "system input" to both the ST and the FD. This is based on the fundamental assumption that the quality and hydrological characteristics of the initial runoff from each of the catchments were essentially the same. The hydrological aspects of the assumption were validated by comparison between UTR flow rates and volumes and corresponding ST data. There are no appreciable in-system losses from the ST, and comparisons showed that flow rates and volumes were generally with ±10% (Ofori, 1984a). It was clearly not possible to validate the quality aspects of this assumption within the scope of the present work, but, as discussed in section 2.1, the overall characteristics of the catchments (and especially, in this context, their limited size and contiguous nature) virtually eliminated the possibility of any serious environmental variations between them, so this assumption was considered entirely justified. One possible exception to this would have been the spillage of vehicular loads on only one of the catchments, but this did not occur during the sampling

period (Butters, 1985). In the UTR sieve solids data presented in section 5.5.4(c), it was noted that fragments of coal and brick, presumably derived from lorry loads, were occasionaly found in the meshes, but these would probably have been derived from continuous in-transit losses and would have affected all catchments equally.

## 7.2 Results and Discussion

### 7.2.1 French Drain Effluent

#### (a) Sieve Solids Sampling and Calculation of Removal Efficiencies

Between March and September 1981 seven sieve solids sampling runs were carried out simultaneously at both drains, and the data arising from these is presented in Table 7.1. Sampling run numbers are the same as those used in section 5.5.4(c). Six mesh sizes (1600, 400, 318, 253, 154 and 100 μm) were used for all UTR runs except the last one (1600 and 400 μm only). For the FD, the precaution was taken of starting with a 400 μm minimum mesh size and only using the next size down if no blockage had occurred during the preceding sampling run. No blockage in fact occurred during any run, and the minimum size was progressively reduced as shown in the table. This precaution was taken to avoid interference with the water sampling and flow measurement arrangements at this location which would have occurred had blockage taken place.

During the second and third sampling periods, blockage occurred of the 400 and 318 μm UTR sieves respectively. The minimum weight that was already trapped on the sieves before blockage was estimated for each of the sizes by finding the lowest weight to cause blockage from all sampling runs, and then to use the nearest "unblocked" weight below that figure. (Data from other UTR sampling runs (excluding the FD) as well as those given in Table 7.1 were used for this purpose). Removal efficiencies in these cases have accordingly been given as minimum values.

TABLE 7.1 : Sieve solids data for untreated runoff and french drain effluent

| Sampling Run Number | No. of Events | Comparison Mesh Size | Untreated Runoff | | | French Drain | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Volume | Wt. of Solids | FWM* Concn. | Weight of Solids Found | Volume[c] | FWM* Concn. | Removal Efficiency |
| | | (μm) | (l) | (g) | ($mgl^{-1}$) | (g) | (l) | ($mgl^{-1}$) | (%) |
| SS2 | 22 | 400 | 31800 | 811.08 | 25.5 | 0.24 | 19900 | 0.012 | >99.9 |
| SS4 | 8 | 400 | 12100 | >175.62[a] | >14.5 | 0.06 | 7070 | 0.008 | >99.9 |
| SS5 | 16 | 318 | 30200 | >189.36[a] | >6.3 | 10.20 | 22000 | 0.464 | >92.6 |
| SS6+7[d] | 5 | 253 | 5070 | 59.71 | 11.8 | 0.24 | 1440 | 0.167 | 98.6 |
| SS8 | 1 | 154 | 2100 | 41.47 | 19.7 | 0.02 | 280 | 0.071 | 97.6 |
| SS10 | 5 | 100 | 4990 | 267.82 | 53.7 | 0.04 | 460 | 0.087 | 99.8 |
| SS11 | 5 | 400[b] | 13000 | 229.65 | 17.7 | 5.74[b] | 9070 | 0.633 | >96.4 |

a = UTR sieve blocked
b = FD mesh size 100 μm
c = estimated from UTR flow data
d = data from two runs combined
*FWM = flow weighted mean

The weight of UTR and FD solids given in Table 7.1 for each run is the cumulative weight of solids found on each mesh down to, and including, the size given under the heading "Comparison mesh size". This size corresponds to the smallest mesh size used simultaneously at the FD and UTR drains. Removal efficiencies for the FD were calculated on the basis of FWM values derived from these comparison mesh size weights by dividing the UTR and FD solids weights by the respective volumes of runoff passing through two sets of sieves. Since FD hydrographs were not, however, available for all sampling runs, due to instrument failure, total volumes of flow from the FD during each run were estimated using UTR data. These estimated volumes could not as they stood be assumed to be equal to the actual FD volumes, however, since comparison of FD and UTR hydrographs for some of the events sampled revealed a noticeable time lag in FD flow initiation compared with UTR, and also that FD event volumes were often substantially lower or sometimes undetectable compared with the corresponding UTR volumes. A build-up volume (maximum ~1750 l) was usually required before FD flow began, and this clearly indicated that losses from the base of the drain were taking place between events. These losses were therefore taken into account when estimating FD volumes using a relationship between antecedent dry period and build-up volume derived by Ofori (1984a):

$$\text{Build up volume} = 460\ (\text{Dry Period})^{0.285}$$

The implications of these losses for sieve solids data comparisons is discussed in conjunction with the results in the section following.

(b) Removal Efficiencies

Table 7.1 shows that for all seven sampling runs, solids removal efficiencies were in all cases extremely satisfactory for the minimum particle sizes considered. Although on two occasions (runs SS5 and SS11) much larger amounts of solids than normal were found on the FD sieves, from visual inspection these appeared to consist of small pieces of gravel removed from the bed itself during exceptionally large events which took place during those runs. Generally, however, the very small amounts of solids that were usually found were fine, discrete gravelly particles, which also appeared to originate

mainly in the granular bed itself, rather than on the road surface. Significantly, almost no trace of the oily agglomerates so ubiquitous in UTR were found on any of the sieves, indicating clearly that the FD was particularly effective in removing this kind of material.

Calculation of the removal efficiencies given in Table 7.1 is based on the implicit assumption that the solids contents of the "lost" volumes in the FD were similar to those actually sampled at the FD outlet. This would hold provided that, during each event, the solids concentrations in incoming runoff were always reduced to a uniformly low level before leaking away or being sampled. This could not of course be verified directly, but two considerations indicate that the effects of the assumption not holding would not have been of great importance. They are:

(a) In all sampling runs but one a series of events was sampled, so build-up volumes were therefore variable and in some cases almost zero where events took place in close succession.

(b) Suspended solids often did not exhibit a first flush behaviour but were basically flow dependent (section 5.5.4), so that peak solids input and therefore a possible peak in effluent solids concentrations may have occurred in cases after the build-up volume was complete.

The combination of these two factors means that the lost volume may at times have contained a lower solids concentration than that passing through and at others a higher one. Over the long-term sampling period covering 62 events, it is likely that these effects would have tended to cancel each other out, thereby making the initial assumption reasonably correct and thus justifying the calculation of solids removal efficiencies on the FWM basis chosen. This basis is also clearly preferable to comparisons on the basis of absolute loads of solids found on the sieves, since the effects of volume losses are catered for.

Table 7.1 also indicates that, excluding the two exceptions previously referred to (runs SS5 and SS11), there was no obvious tendency in the remaining five runs for the removal efficiency to decrease with decreasing mesh size down to 100 μm, indicating that

fine as well as coarse particles in the size range sampled are efficiently removed. The corresponding FD FWM values for these runs are considered sufficiently low compared with the initial UTR values to confirm that, for the size range considered, any differences in TSS concentrations between "lost" volumes and sampled effluent are insignificant compared with the degree of solids removal achieved.

(c) Wider Comparisons with Untreated Runoff

In order to gain a broader picture of FD effectiveness, solids removal efficiencies have also been compared on the basis of UTR and FD event flow weighted mean (FWM) concentration values. The UTR TSS values used are the same as those presented in section 5.5.5, and the FD values arise from events sampled during the corresponding winter or summer periods, some simultaneously with those sampled for UTR. Comparisons have therefore been carried out for winter and summer periods separately by comparison (t-test) of the TSS seasonal means derived from UTR and FD event data, in a similar manner to that used for comparison of UTR seasonal means in section 5.5.5. These data are presented in Table 7.2 along with analogous values for Pb, Zn and $Cl^-$ in order to facilitate broad comparisons between these and TSS data. Removal efficiencies, calculated on the basis of FWM mean values, have also been presented. As in section 5, TSS and Pb FWM values for summer event S8 have been excluded from comparisons.

Examination of the TSS removal efficiencies presented in Table 7.2 shows that despite the trends to considerably higher TSS FWM concentrations in summer UTR, the corresponding FD FWM value is about half that found in winter. As noted in section 5.5.5, the higher summer UTR values are probably due to increased mobilisation of heavier solids from the road surface by the higher mean flows (Table 5.2). These solids will be more easily settleable and therefore more easily removed by the FD than the finer solids which predominate in winter, and thus overall removal efficiencies will tend to be higher in summer (Table 5.2).

Other factors which may also have influenced seasonal differences are the probable presence of fine solids from de-icing salt in many winter events, as noted in section 5.5.3(b), and a slight trend to higher event mean volumes in summer (section 5.2.2(c)). In the

TABLE 7.2 : Comparisons between untreated runoff and french drain effluent

| | TSS ($mgl^{-1}$) | Pb ($\mu gl^{-1}$) | Zn ($\mu gl^{-1}$) | $Cl^-$ ($mgl^{-1}$) |
|---|---|---|---|---|
| WINTER | | | | |
| UTR ( Mean | 171 | 649 | 1168 | 1364 |
| UTR ( RSD (%) | 39.2 | 48.7 | 84.9 | 128 |
| UTR ( n | 12 | 9 | 9 | 10 |
| FD[a] ( Mean | 56.3 | 235 | 200 | 677 |
| FD[a] ( RSD (%) | 38.4 | 53.1 | 37.0 | 52.7 |
| FD[a] ( n | 8 | 8 | 7 | 8 |
| Reduction (%) | 67 | 64 | 83 | 50 |
| Significance of difference between means | >0.99 | >0.99 | >0.98 | <0.9 |
| SUMMER | | | | |
| UTR ( Mean | 285 | 751 | 1091 | 16.7 |
| UTR ( RSD (%) | 83.1 | 50.5 | 49.6 | 61.3 |
| UTR ( n | 11 | 7 | 7 | 12 |
| FD[a] ( Mean | 25.4 | 43.0 | 160 | 43.4 |
| FD[a] ( RSD (%) | 48.0 | 47.4 | 78.1 | 98.2 |
| FD[a] ( n | 9 | 8 | 9 | 8 |
| Reduction (%) | 91 | 94 | 85 | 0.0 |
| Significance of difference between means | >0.99 | >0.99 | >0.98 | <0.9 |
| Mean reduction (winter and summer, %) | 79 | 79 | 84 | 25 |

[a] = data from Ofori (1984b)

former case, the salt-derived fine solids were estimatd to be able to produce an overall seasonal flow-weighted mean TSS concentration of up to 20 $mgl^{-1}$, which is 36% of the winter FD FWM concentration. Thus, if the majority of these solids were not retained by the FD in winter, their absence in summer events would undoubtedly have contributed to the lower summer FWM value at this drain. The trend towards higher event mean volumes for sampled events in summer may also have caused some "dilution" of UTR fine solids in summer compared with winter, and this would also tend to emphasise the effect of removal of larger particles on summer removal efficiencies.

As with suspended solids removal efficiencies presented for the sieve solids data, the foregoing comparisons are implicitly based upon the assumption of the comparability of lost and sampled effluent, and thus the effect of departures from this must be also be taken into account in the present case. The variation in build-up volume and the variability of the time of occurrence of peak TSS input concentrations during events, which were considered to reduce the effect of this when sieve sampling of a sequential series of events, can, however, be considered to apply to an approximately similar extent to random sampling of a number of individual events, which the data in Table 7.2 are derived from. In the light of this, comparison of FD effluent quality and UTR on the basis of FWM mean values for TSS (and strongly solid-associated contaminants) is considered reasonable.

The sieve solids data given in Table 7.1 were, with one exception, obained during the summer sampling period, and therefore comparison with the TSS data in Table 7.2 will be restricted to that period. On the basis of these two sets of data, it is clear that the French drain is generally better than 97% efficient in removing solids $\geq$ 100 µm, compared with a mean value of 91% for all suspended solids (Table 7.2). Since the removal efficiency of the drain shows no tendency to decrease with decreasing size of sieve mesh down to 100 µm, comparison of the $\geq$97% figure with the 91% value suggests that the approximately 6% difference between the two figures can be accounted for by solids in the $<$100µm range which are not trapped by the sieves. Additionally, the high removal efficiency for particles $\geq$100 µm means that the contribution to the overall TSS concentrations in FD effluent of this size fraction is negligible (mean 0.21 $mgl^{-1}$). Thus the mean

summer TSS value of 25.4 $mgl^{-1}$ can reasonably be assumed to consist of particles of <100 μm size, and this value is 9% of the UTR summer TSS mean, which is comparable to the 6% difference in removal efficiency figures noted above.

As expected, the removal efficiency data for Pb indicate a close similarity with TSS data, and again reflect the substantially solid-associated nature of this parameter. Although the degree of Zn solid-association was shown in section 5.5.6(a) to be much more variable than for Pb, the removal efficiencies found are still substantial, and may indicate some adsorption of dissolved Zn on the granular media (Peters and Perry, 1983). In addition, Zn is more closely associated with soluble $Cl^-$ movement in the winter months (section 5.6.3(d)), and there was some evidence in the composite sample Zn data from this season for a first flush effect. This may have led to a greater proportion of the dissolved Zn loads being removed in the build-up volumes than in the case with more solid-associated Pb, and this would also explain the apparent trend to higher Zn removal than for Pb which occurs in winter. The $Cl^-$ data for winter is predictably dominated by de-icing salt effects, but the summer data indicate clearly that the removal of soluble major anions (including $Br^-$) in runoff by the FD can be expected to be minimal.

Although sufficient oil and PAH data were not available from UTR or FD effluent to permit examination of removal efficiencies on an FWM basis, the close association of these parameters with TSS can be used to estimate an approximate figure for removals. Concentrating on summer data in order to exclude the effects of salting solids, application of the mean solid-associated oil concentration figure of 72 mg $g^{-1}$ (derived in section 5.5.9(b)) to the summer UTR and FD mean TSS FWM values of 285 and 25.4 $mgl^{-1}$ (Table 7.2) leads to related solid-associated oil concentrations of 20.5 and 1.8 $mgl^{-1}$ respectively. Overall removal efficiency must take into account the dissolved oil fraction, given by Pope *et al.* (1978a) as ~10% of the total. This figure would indicate a dissolved oil UTR FWM of 2.3 $mgl^{-1}$, giving a total UTR FWM of 22.8 $mgl^{-1}$. Assuming no removal of dissolved oil, the total FD effluent FWM would then be 4.1 $mgl^{-1}$, i.e. an overall removal efficiency of 82%. Assuming for the purposes of this estimate that the mean sieve solids PAH/oil ratio of

$0.43 \times 10^{-3}$ (Table 5.9) applies to both solid-associated and soluble PAH fractions, this leads to UTR and FWM PAH means of 9.8 and 1.8 $\mu g\ l^{-1}$ respectively for the six PAH considered. Removal efficiencies in winter may be reduced, following the trends for TSS and Pb, and in general will clearly depend on the degree of solid association, but the FD sieve solids data shows unambiguously that the solid-associated oil removal for particles down to 100μm is effectively complete.

### 7.2.2 Sedimentation Tank Effluent

#### (a) Sieve Solids Sampling

Three sampling runs were carried out between April and June 1981. The data are summarised in a similar manner to those from the FD, in Table 7.3, except that, because of the similarity of volumes recorded at the UTR and ST drains, no adjustments for losses were necessary. As with the FD, the original intention was to use a 400 μm mesh for the first run and then use progressively lower sizes, but due to blockage problems even with this size, no smaller mesh was used. After three runs it became clear that blockage could occur very easily, and no further sampling was carried out, in order to avoid interference with water sampling and flow monitoring. FWM solids concentrations were calculated as for FD data.

The significance of the occurrence of the blockage problem was that this was always caused by a film of the oily agglomerate which was noticeably absent from the FD sieve solids. Since the weights of solids trapped in three ST runs were within the range found on the FD sieves, however, the occurrence of the blockage problem does not necessarily mean that the solids removal efficiency within the $\geq$ 400 μm size range was drastically worse than that of the FD, as is indicated by the data for the first two runs. (The third run covered a relatively small volume of runoff giving rise to an exceptionally low solids load in the UTR sieves). Nonetheless, this occurrence suggests strongly that the sedimentation tank was not as effective as the FD in removing the kind of oily, non-settleable solid material which was very apparent in UTR, and points to the necessity of using some kind of oil separator in any sedimentation-based runoff treatment system which is to be truly effective in this respect.

TABLE 7.3 : Sieve solids data for untreated runoff and sedimentation tank effluent

| Sampling Run Number | No. of Events | Comparison Mesh Size | Untreated Runoff | | | Sedimentation Tank | | |
|---|---|---|---|---|---|---|---|---|
| | | | Volume | Wt. of Solids | FWM* Concn. | Weight of Solids | FWM* conc. | Removal |
| | | (μm) | (l) | (g) | ($mgl^{-1}$) | (g) | ($mgl^{-1}$) | (%) |
| SS3 | 1 | 400 | 3660 | 88.95 | 24.30 | 3.70 | 1.01 | 95.8 |
| SS5 | 16 | " | 30200 | >122.45[a] | >4.05 | >3.41[a] | ~0.11 | ~97.0 |
| SS7 | 4 | " | 2720 | 3.67 | 1.35 | 1.50 | 0.55 | 59.3 |

[a] = Sieves blocked - approximate removal efficiencies calculated from these weights
* = Flow weighted mean

(b) Wider Comparisons with Untreated Runoff

In a similar manner to that adopted for the FD in the previous section, ST performance has also been compared with UTR on a wider basis, using FWM data from seven events sampled during the same period as the present work. The data resulting from this are presented in Table 7.4. As before, UTR data is the same as that presented in section 5.5.

For winter comparisons, a major feature is the much lower TSS removal efficiency compared with that found for the FD, although the difference between ST and UTR means is still significant at the $P > 0.95$ confidence level. This trend indicates that, compared to the FD, the ST is relatively ineffective in removing the finer solids which predominate in winter runoff. As with the FD, however, summer TSS removal efficiencies are substantially higher, probably due to basically similar reasons, but again the degree of removal is not generally as high as that achieved by the FD. Because of limited sieve solids data from this drain, comparisons with Table 7.4 can only suffice to indicate that removal of settleable solids $> 400$ µm is probably satisfactory. Seasonal differences in removal efficiencies for Pb and Zn follow similar trends to those for TSS, although the lower summer Zn removal compared with Pb may indicate the absence of Zn adsorption by granular media, which was previously suggested as taking place in the FD. As anticipated, winter $Cl^-$ data is again dominated by de-icing effects, but summer data indicates that, as with the FD, removal of soluble major anions is effectively zero.

An assessment of the oil and PAH removal efficiencies for summer conditions was also carried out on a similar basis to that adopted for the FD (section 7.2.1(c)), and led to ST FWM oil and PAH values of 5.5 $mgl^{-1}$ and 2.4 $\mu gl^{-1}$ respectively, giving removal efficiencies of 76%. As with the FD, this value is likely to be lower in winter, but to a greater extent, and, as noted previously with respect to the sieve solids data, removal of non-settleable solid-associated oil is clearly not as highly efficient as with the FD.

In conclusion, therefore, it is apparent that the FD is generally more effective at removing suspended solids and associated contaminants from motorway runoff, while neither the FD nor the ST

TABLE 7.4 : Comparisons between untreated runoff and sedimentation tank effluent

| | TSS ($mgl^{-1}$) | Pb ($\mu gl^{-1}$) | Zn ($\mu gl^{-1}$) | $Cl^-$ ($mgl^{-1}$) |
|---|---|---|---|---|
| WINTER | | | | |
| UTR ( Mean | 171 | 649 | 1168 | 1364 |
| UTR ( RSD (%) | 39.2 | 48.7 | 84.9 | 128 |
| UTR ( n | 12 | 9 | 9 | 10 |
| ST[a] ( Mean | 112 | 505 | 663 | 710 |
| ST[a] ( RSD (%) | 27.1 | 24.9 | 14.2 | 61.0 |
| ST[a] ( n | 4 | 4 | 4 | 4 |
| Reduction (%) | 34.5 | 22.2 | 43.2 | 47.9 |
| Significance of difference between means | >0.95 | <0.9 | <0.9 | <0.9 |
| SUMMER | | | | |
| UTR ( Mean | 285 | 751 | 1091 | 16.7 |
| UTR ( RSD (%) | 83.1 | 50.5 | 49.6 | 61.3 |
| UTR ( n | 11 | 7 | 7 | 12 |
| ST[a] ( Mean | 43.8 | 136 | 364 | 48 |
| ST[a] ( RSD (%) | 29.5 | 40.0 | 7.9 | 93.6 |
| ST[a] ( n | 3 | 3 | 3 | 3 |
| Reduction (%) | 84.6 | 81.9 | 66.6 | 0.0 |
| Significance of difference between means | >0.99 | >0.99 | >0.98 | <0.9 |
| Mean reduction (winter and summer, %) | 59.6 | 52.1 | 54.9 | 24.0 |

[a] = data from Ofori (1984b)

have much effect on soluble anions. The FD also appears to be more effective at removing non-settleable oily solids than the ST.

## SECTION 8. GENERAL DISCUSSION

The results of the present work have made it clear that stormwater runoff from a highway surface is often of sufficiently poor quality to warrant serious concern over its effects on receiving waters, whether these are streams in rural catchments traversed by highways or waters receiving stormwater runoff from an urban catchment.

The precise contribution of highway surfaces to the stormwater runoff quality of an urban area will clearly depend on many local factors, particularly the area of road surface relative to the area of the catchment as a whole. A general indication of the potential contribution can be gained, however, by comparing concentrations and loadings from the present work with similar data for separately sewered urban stormwater runoff from several UK catchments, collated by Mance (1982). Figures 8.1A and B presents Mance's data along with that from the present work. From Figure 8.1A it is clear that, in comparison with concentrations of suspended solids, $Cl^-$, COD, total Pb and total Zn from most of the urban catchments, those found in runoff from the M1 site are often substantially higher, although all non-road surfaces (e.g. roofs, pavements, etc.) which could also contribute contaminants to runoff from the urban areas included are entirely absent from the M1 catchment. This tends to confirm, therefore, the predominantly vehicle and road-related nature of many of the pollutants concerned, and in the present work, consideration of specific sources of Pb, Zn, $Cl^-$ (and $Br^-$) has emphasised this in these cases. Significantly, the only catchment in Fig. 8.1A for which concentration values available are higher than in the present work (Graham's Park, Hendon, London) contains a 3.3 km stretch of the M1 and lengths of other major roads (Ellis, 1979), and Mance (*op. cit.*) suggests that this could have been one of the factors contributing to the higher concentrations found.

The unit area loading data on Fig. 8.1B further clarifies the comparison between M1 runoff quality and urban runoff quality generally. As expected, variation within the data is reduced in some cases, but for COD, $Cl^-$, total Pb and total Zn unit area loadings from the M1 site are all higher than any of the available values from the urban sites. For suspended solids, the M1 value is again second only to the Graham's Park figure and is probably again indicative of the

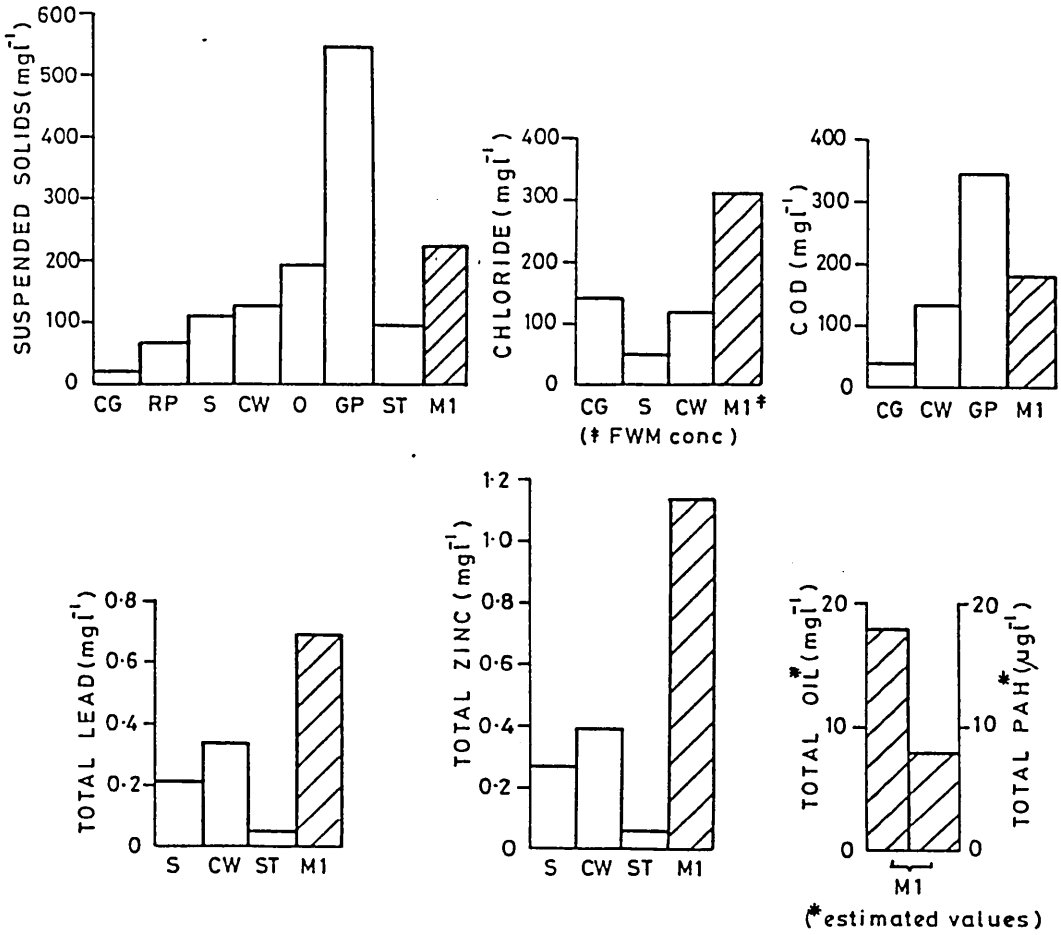



Figure 8.1A Pollutant mean concentrations in separately sewered urban stormwater runoff from UK catchments compared with M1 data (Key: CG = Clifton Grove; RP = Rise Park; S = Shephall; CW = Chelmsley Wood; O = Oxhey; GP = Graham's Park; ST = Stevenage. Catchment details and derivation of M1 data are given in Appendix 10)

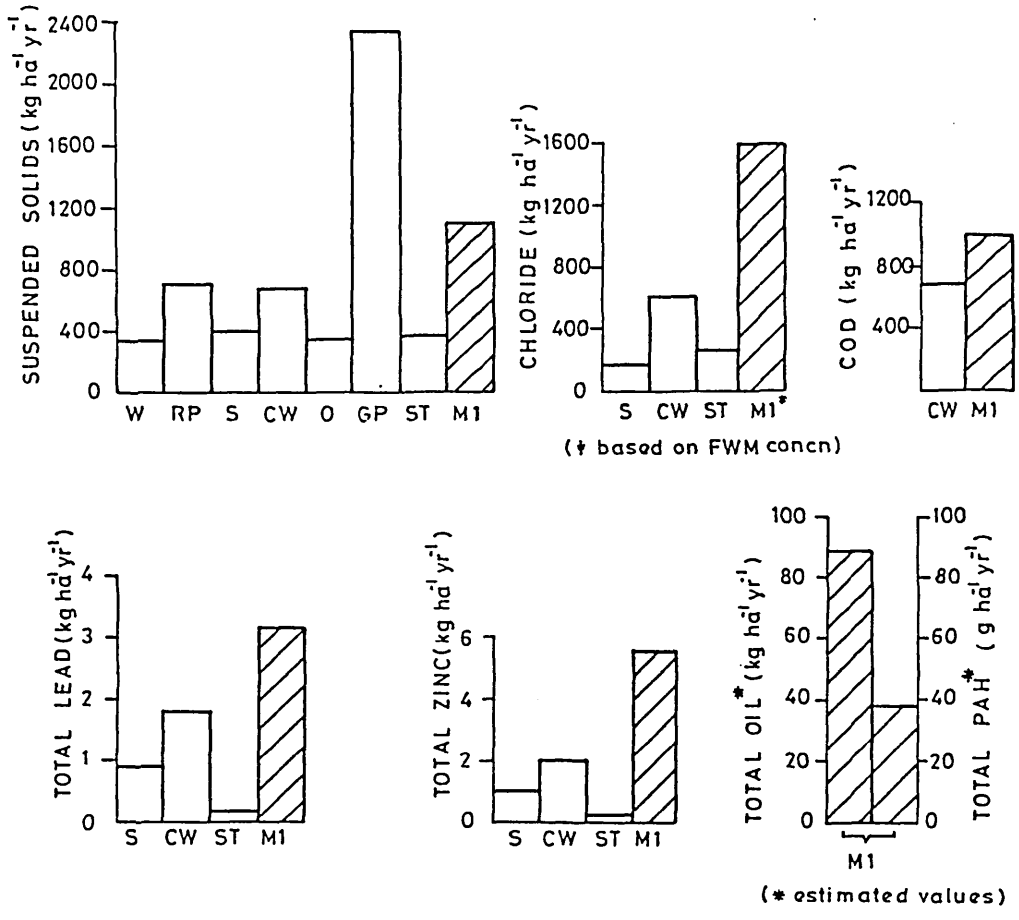



Figure 8.1B Annual unit area pollutant loadings in separately sewered urban stormwater runoff from UK catchments compared with M1 data (Key: W = Welbeck; remainder as for Fig. 8.1A)

effect of the highway areas in this latter catchment. It is also noteworthy that all of the catchments (M1 excluded) in Figs 8.1A and B are part of a wider urban or suburban area, and would therefore be expected to receive a greater contribution from atmospheric deposition to stormwater pollutant loadings than would the rural M1 site. This contribution was estimated to be in the region of 25% for chloride and SS in the Stevenage catchment (Mance and Harman, 1978). The general absence of this at the M1 site is clearly compensated for by the higher loadings from the catchment itself, and emphasises the dominant contribution which road surfaces alone can make to urban stormwater pollutant loadings.

Although urban runoff is increasingly recognised as containing high concentrations of oil and PAH (Stenstrom et al., 1984), no data for these parameters were available for any of the urban catchments included in Figures 8.1A and B, but concentrations and loading data for these from the M1 site (estimated from TSS data in a similar manner to that given in section 5.5.9) have been included to demonstrate the levels which might be expected. Comparisons for oil can, however, be made on a unit area loading basis with the data from Söderlund and Lehtinen (1972) in Table 1.2, from which it is evident that annual loads for residential areas were in the range 2.6-6.6 kg $ha^{-1}yr^{-1}$, considerably lower than the M1 estimate of 89 kg $ha^{-1}yr^{-1}$. Söderlund and Lehtinen's own figure for a highway area, 13.4 kg $ha^{-1}yr^{-1}$, is also noticeably higher than the residential area data, although considerably lower than the M1 estimate. As noted in section 1.1.2, Hoffman et al. (1984) also indicated similar trends for PAH. Although extensive data for oil and particularly PAH in motorway and urban runoff is not generally available, such evidence as exists clearly indicates therefore that these are characteristic and significant contaminants of motorway runoff, and in general road surfaces may contribute a substantial proportion of the total runoff load from an urban area. Clark et al. (1984) have indicated that an increase in the aromatic content of petrol in the UK following a reduction of the Pb content in January 1986 may lead to an increase of PAH in urban atmospheres, and this may in turn further increase the loadings in urban runoff.

As noted in section 1.1.1, the impact of motorway runoff in rural catchments in the UK appears to have received little study to

date, yet in view of the widespread use of such catchments (lowland and upland) for raw water supplies the problem is worthy of serious consideration, especially in view of the higher degree of imperviousness and consequent rapidity of rainfall-runoff response of highway surfaces compared with rural land areas generally. General comparisons of annual rural and highway catchment loadings for some parameters can, however, be made with the work of Sonzogni et al. (1980) who presented data from a large-scale study of runoff quality from several different types of catchment (e.g. urban, agricultural) in the Great Lakes area of the US. The comparisons are given in Table 8.1, and it is clear from these that although suspended solids loads from rural catchments can sometimes exceed those from the M1 site, loadings of Pb, Zn and $Cl^-$ are far greater than the rural range. No oil and PAH data were given by Sonzogni et al. (op. cit.), and in general such data for non-urban areas appear to be very scarce, but the contrasts between residential and highway area oil and PAH loadings previously noted suggests that rural area loadings will generally be far lower than for highway surfaces. These contrasts therefore emphasize that the contribution of a highway surface to these pollutants in a rural area may be out of all proportion to the ratio of highway area to pervious areas in some locations. Such considerations have already played a part in discussions concerning the proposed route of an interstate highway in the northeastern USA, where contamination of potable supply watersheds following highway construction is feared (Adams, 1981).

The polluted nature of motorway runoff found in this study was also apparent in other UK studies of this topic noted in section 1.1, and it can be assumed therefore that most runoff from UK motorways will be of a broadly similar quality, within the inevitable variations caused by local circumstances. In view of the considerable expansion of the UK motorway system within the last two decades, this must be a cause for concern, particularly in view of the trend to more extensive and stringent statutory limits on contaminants in discharges to receiving waters, partly as a result of EEC legislation. In the United Kingdom, however, no pollutants discharged to a water course (stormwater included) are subject to single fixed statutory limits on concentration, but for treated sewage, the recommendations of the 1912

TABLE 8.1 : Comparisons of annual unit area loads from the M1 catchment and US rural areas
(Rural data after Sonzogni et al., 1980)

| Land Use | Parameter (kg $ha^{-1}yr^{-1}$) | | | |
|---|---|---|---|---|
| | Suspended Solids | Lead | Zinc | Chloride |
| General agriculture | 3-5600 | 0.002-0.08 | 0.005-0.3 | 10-120 |
| Cropland | 20-5100 | 0.005-0.006 | 0.026-0.083 | 10-50 |
| Pasture | 30-80 | 0.004-0.015 | 0.019-0.172 | NA |
| Forest/wooded | 1-820 | 0.01 -0.03 | 0.01 -0.03 | 2-20 |
| Fallow | 7-820 | 0.01 -0.03 | 0.01 -0.03 | 20-35 |
| M1 catchment | 1109 | 3.16 | 5.65 | 1603 |

NA = not available

Royal Commission on Sewage Disposal (Eighth Report) have been very widely adopted (Tebbut, 1983). The Commission recommended a maximum BOD value of 20 $mgl^{-1}$ and a value of 30 $mgl^{-1}$ for SS, limits which, for BOD, were based on a minimum assumed dilution of 8:1 with stream water with a BOD of 2 $mgl^{-1}$. BOD was not measured in this work, but the flow-weighted mean TSS concentrations in Fig. 5.13 can be usefully compared with the 30 $mgl^{-1}$ standard. Comparison shows that, excluding event S8, this standard was violated by factors ranging between 1.7 and 24 times. It is clear that, to comply with the 30 $mgl^{-1}$ standard, all the storm runoff monitored would require dilution by a factor often considerably greater than eight.

In addition, for some industrial discharges containing specific materials such as Pb, Zn or oils, water authorities may require higher standards to be met in certain locations. The Anglian Water Authority, for instance, limits oil concentrations in discharges to unpolluted (class 1 ) streams to 2 $mgl^{-1}$, assuming dilution of 8:1 (Peters, 1985). Concentrations in motorway runoff may at times be considerably higher, however, and where motorways traverse a rural catchment, this dilution requirement may not always be met, especially during summer when receiving water flows are frequently low. In such instances, because of the trend to more intense storms during this period and the relatively rapid response of a highway catchment, large

volumes of highly polluted water may be discharged to a water course within a relatively short period of time, and thus before flows from other parts of the catchment increase the dilution volume available in the stream (Laxen and Harrison, 1977). Under such circumstances motorway runoff may contain higher concentrations of certain materials than those permitted for industrial concerns operating within Water Authority limits.

Until recently, discharges of untreated motorway runoff direct to receiving waters were not generally subject to legal control, but under the terms of the recently implemented Part II of the Control of Pollution Act, 1974, discharges from new motorway developments will now have to meet water authority consent conditions (Colwill, 1985), although existing discharges will be allowed to continue. At present, it is too early to discern the long term impact of this change, but it is apparent that the sporadic and highly variable nature of stormwater runoff will make monitoring and compliance with standards a difficult task.

Although nationwide rigid concentration standards are not applicable to effluents in the UK, raw waters which are used for potable supply abstraction are subject to the EEC limits laid down in the "Directive Concerning the Quality Required of Surface Water Intended for the Abstraction of Drinking Water" (Council of the European Communities, 1975), applicable to all member states. Appendix 11 presents the standards and relevant definitions. Most of the parameters examined in the present work are included in the Directive, and a comparison of the Directive's limits with concentrations of these parameters in runoff from the M1 site is given in Table 8.2. As noted in Appendix 11, the limits are varied according to the level of treatment available, and are generally stricter where only minimum treatment is possible, so comparisons have been made on the basis of standards applicable where "minimum" and "intensive" treatments are available. No data for Br have been given since this is not included in the Directive.

Inspection of Table 8.2 reveals that, for Pb, Cd, COD, PAH and Cl, significant dilution of the highest event means recorded would be required before receiving water standards could be met, with Pb, as

TABLE 8.2 : Comparison of runoff contaminant concentrations found in the present work with 1975 EEC Surface Water Directive (Appendix 11)

| Parameter | | Minimum Treatment (A1)[a] | | | Intensive Treatment (A3)[a] | | | Highest[c] Event Mean (HEM) | HEM diln* needed to meet A3 Limit (I or G[b]) |
|---|---|---|---|---|---|---|---|---|---|
| | | Guideline Limit (G) | Mandatory Limit (I) | % of Flow Exceeding I (or G)[b] | Guideline Limit (G) | Mandatory Limit (I) | % of Flow Exceeding I (or G)[b] | | |
| TSS | ($mgl^{-1}$) | 25 | - | 100 | - | - | - | 723 | - |
| Lead | ($mgl^{-1}$) | - | 0.05 | 100 | - | 0.05 | 100 | 1.5 | x30 |
| Zinc | ($mgl^{-1}$) | 0.5 | 3.0 | none | 1 | 5 | none | 3.5 | none |
| Cadmium | ($mgl^{-1}$) | 1 | 5 | i.d. | 1 | 5 | i.d. | 76 | x15 |
| COD | ($mgl^{-1}$) | - | - | - | 30 | - | 100 | 340 | x11 |
| Soluble Hydrocarbons | ($mgl^{-1}$) | - | 0.05 | i.d. | 0.5 | 1 | i.d. | ~6[e] | x6 |
| PAH ('WHO 6') | ($\mu gl^{-1}$) | - | 0.2 | i.d. | - | 1 | i.d. | ~25[e] | x25 |
| PAH (B(a)P) | ($\mu gl^{-1}$) | - | 0.2 | i.d. | - | 1 | i.d. | ~5[e] | x5 |
| Chloride | ($mgl^{-1}$) | 200 | - | 14 | 200 | - | 14 | 5590 | x28 |
| Conductivity | ($\mu S\ cm^{-1}$) | 1000 | - | 16 | 1000 | - | 16 | 22000[d] | x22 |

a = for details of treatment levels, see Appendix 11
b = guideline limit used where no mandatory limit given
c = from FWM data in Appendix 6
d = individual sample
e = estimated from sieve solids oil/PAH data
i.d. = insufficient data
* = dilution

might be expected, requiring the highest degree of dilution. Concentrations of Zn found, however, do not appear to give cause for serious concern in this context. Both Pb and COD FWM concentrations exceeded the limits for all events sampled, and it appears probable that the same would apply to PAH concentrations. In practice, however, it is likely that concentrations of solid associated contaminants such as Pb and PAH would be substantially reduced by sedimentation shortly after discharge, and it is thus unlikely that in most locations the standards for these constituents would be violated at the point of abstraction due to motorway runoff alone. Nonetheless, the prominence of Pb, COD and PAH (and in some cases possibly TSS) among those parameters requiring the highest theoretical dilutions to meet the EEC standards recalls the contrast between the high loadings of these parameters in motorway runoff and those found in domestic sewage, which was noted by Klein (1982) and Dauber et al. (1978), and is an additional reminder that Pb, hydrocarbons and PAH are among the most characteristic pollutants in highway runoff.

Although solid-associated contaminant concentrations in motorway runoff water may be reduced by settlement, soluble constituents will not be affected and thus dilution will be of much greater importance. Chloride is clearly one of the most important soluble contaminants in motorway runoff in winter months, and although in the present work only for 14% of sampled flow were concentrations above the EEC limit (Table 8.2), in wider terms it is nonetheless significant that, in contrast to the other parameters in Table 8.2, $Cl^-$ from de-icing salt has led to specific instances of impairment of water supplies in the UK, as noted in section 1.1.2(c). As shown in the present work, this may also be a significant source of $Br^-$ in motorway runoff waters, and an assessment of this problem for some specific locations is discussed shortly.

The possible inadequacy of available dilution to mitigate the effects of motorway runoff pollution points to the necessity of some form of treatment for discharge of this type if receiving water quality is to be effectively safeguarded at all times. It must be recalled, however, that, unlike untreated runoff in this work, runoff from motorways in most locations in the UK is drained from the road surface by means of gully pots and culverts, or by a french drain

arrangement. The latter may also have been installed in some locations to act as a subsurface drain (Bartlett, 1981). Thus motorway runoff is generally already subject to some form of "treatment", and assessing the efficacy of treatment systems and recommending possible improvements on the basis of the present work must take this factor into account.

In the light of this, the data presented in section 7, concerning french drain solids removal efficiencies, indicated clearly that effluent from this type of drain is unlikely to seriously contravene present water quality standards for suspended solids and strongly solid-associated pollutants. Runoff from motorways where such drains are already installed therefore appears likely to be already receiving an adequate degree of solids removal treatment, provided that their working life of 5-7 years (Spalding, 1970) has not been exceeded. Where gully pots are the main mode of surface drainage, however, the effectiveness of these in treating road runoff must be open to considerable doubt, as the literature reviewed in section 1.3 indicated. This is especially so in the present case, since throughout Pope's previous work at the M1 site, gully pots were left as originally installed during motorway construction, and sediment was removed during a routine cleansing operation by the local authority only once during this period (Pope, 1979a). Thus Pope's data might be expected to reflect to some degree the effect of gully pots on motorway runoff quality under realistic operating conditions, when compared with data from the present work. As noted at several points in section 5.5, however, the range of untreated runoff contaminant concentrations found in this work is quite comparable with those found by Pope, and as such there is no clear evidence at all that gully pots caused any real improvement in runoff quality during that period.

Apart from those locations where french drains have already been installed, therefore, on the basis of the present work there appear at present to be three realistic options open to local authorities responsible for motorway drainage who wish to substantially improve the quality of runoff. These are:

(a) More frequent cleansing of existing gully pots.

(b) Replacement of gully pots by sedimentation tanks where possible and sludge removal at reasonable intervals.

(c) Replacement of gully pots by french drains along the edge of the hard shoulder.

The main advantage of option (a) is that no direct capital spending on construction is required, but in view of the very limited resources allocated at present to motorway gully pot cleansing (at present, one cleansing per year in the M1 site area) it would appear that some investment in additional cleansing vehicles and employment of additional labour would be required to implement significantly increased cleansing frequencies. Such investment would, however, carry with it additional current spending requirements, which would have to continue indefinitely if any substantial impact on runoff quality were to be maintained. These penalties would probably appear even more unattractive, however, when set against the previously noted evidence indicating the limited effects of gully pot in improving runoff quality (section 1.3). Because of this, such an approach would probably be least effective in reducing the fine sediment load which is of considerable importance in terms of pollutant removal and dispersion from highway surfaces.

In the light of these factors, option (b), installation of sedimentation tanks in place of gully pots, has several advantages. The simple design and construction of the tank used in the present work means that construction costs would be relatively low if such a design were widely adopted, and although sludge would accumulate slowly at the base of the tank, the cleansing intervals required to maintain effluent quality could be kept to a much lower frequency than that required for gully pots in option (a). Thus little or no extra expenditure on equipment or labour over and above present requirements would be necessary.

In spite of these advantages compared with gully pots, however, the data concerning sedimentation tank treatment efficiency (section 7.2.2) indicated clearly that solids removal was significantly lower than that found for the french drain. Because of this, option (c), i.e. french drain installation, would be preferable in water quality control terms to widespread use of sedimentation tanks, although the initial construction costs are likely to be considerably higher. Despite this, additional advantages are that short-term maintenance

requirements are effectively nil, while the additional land area required, consisting only of a narrow (~1 m) strip bordering the hard shoulder, would probably be easily accommodated within existing motorway boundaries in many instances. In contrast to a relatively simple and infrequent desludging operation required for sedimentation tank maintenance, however, long term french drain maintenance may require eventual removal of the granular bed and associated sludge, followed by cleaning and replacement of the bed or replacement by fresh granular material, an operation which would be considerably more expensive than tank desludging. The time interval at which this would have to be done is probably in the region of 5-7 years (Spalding, 1970) but nonetheless the extra expense involved may well be justified by the considerably improved effluent quality achieved with this sytem.

Apart from the considerations discussed above, an additional factor which may have to be taken into account in assessing practical aspects of treatment system choice is the question of sludge disposal. More frequent gully pot cleansing or installation of sedimentation tanks coupled with regular desludging would lead to greater volumes of sludge requiring disposal than under present circumstances, where gully pot cleaning is very infrequent. In view of the largely solid-associated nature of such contaminants as Pb, oil and PAH, however, such sludge would undoubtedly contain significant quantities of such materials, and therefore the volumes likely to arise from improved runoff treatment and possible associated disposal problems should at least be considered.

A very approximate estimate of the quantities of sludge which might arise from treatment of runoff from a 1 km length of the M1 can be made based on the annual unit area TSS loading figure from Fig. 8.1B, 1109 kg $ha^{-1}yr^{-1}$, which is equivalent to 1641 kg $km^{-1}$ motorway $yr^{-1}$. Estimates of sludge weights and volumes likely to arise from gully pots and sedimentation tanks (placed every 50 m) from one km in one year have been made, based on the following assumptions:

(a) Mean annual sedimentation tank solids removal efficiency is 60% (section 7.2.2).

(b) Mean annual gully pot solids removal efficiency is 20% (based on work by Pratt and Adams (1984) and assuming regular cleansing to maintain this efficiency).

(c) Mean sludge solids content is 0.781 g $cm^{-3}$ (Ofori, 1984a).

The volumes of sludge arising under identical conditions from the length of the M1 in Bedfordshire (24 km, equivalent to 48 km single three lane carriageway) have also been calculated to assess the quantities likely to be dealt with by a specific authority.

The results of the estimates are given in Table 8.3, from which it can be seen that the sludge volumes likely to arise are probably small enough to be dealt with without difficulty in most cases. At present, gully pots are installed at approximately 50 m intervals, and the estimated capacity of these along a 1 km stretch of motorway is 3 $m^3$, which appears sufficient to contain the estimated 0.42 $m^3$ of sludge estimated to accumulate annually. Use of sedimentation tanks may, however, give rise to approximately three times as much sludge requiring disposal than at present.

According to Hawkins (1983), gully pot contents are not classified as hazardous waste and may be disposed of in a similar manner to household refuse e.g. to a landfill site. In the specific case of Bedforshire, however, only a part of M1 gully pot contents are at present disposed of on refuse tips, while the remainder is simply tipped onto a suitable stretch of motorway verge when convenient (Butters, 1985). Such an approach would hardly seem an improvement on present practice if continued in circumstances where motorway runoff received more adqeuate sedimentation than at present, and illustrates that disposal of such sludge may need to be managed with more thought in such cases.

The nature of any sludge disposal problem arising from french drain granular bed renewal is more difficult to assess at present, but complete removal of the bed would probably lead to considerable mixing of accumulated solids and the granular material. The ultimate fate of the solids and associated pollutants would then appear to depend on whether the original bed material was cleaned in some way and then replaced, or renewed entirely. In either case, considerable dispersion of the solids appears possible.

TABLE 8.3 : Sludge accumulation in gully pots and sedimentation tanks

| Treatment Installation | Average Annual Solids Removal Efficiency (%) | Wt. of Solids Accumulated[a] (kg $km^{-1}yr^{-1}$) | Estimated[b] Sludge Volume ($m^3km^{-1}yr^{-1}$) | Sludge Volume from M1[c] in Bedfordshire ($m^3yr^{-1}$) |
|---|---|---|---|---|
| Sedimentation tank | 60 | 985 | 1.26 | 60.5 |
| Gully pots | 20 | 328 | 0.42 | 20.2 |

a = based on annual untreated runoff load of 1641 kg $km^{-1}yr^{-1}$
b = based on mean sludge solids content of 0.781 g $cm^{-3}$ (Ofori, 1984a)
c = length of single three lane carriageway = 48 km

Although considerable solids removal may be achieved by the correct choice of a runoff treatment system, the basic function of all those considered is such that soluble components of runoff are not substantially affected. In this respect, it is to be expected that $Br^-$ in highway runoff, being predominantly in soluble form, will not be significantly reduced by the kinds of treatment previously discussed. From Fig. 6.1, however, it is clear that, in many instances, $Br^-$ concentrations in untreated runoff can be far in excess of those found in unpolluted surface waters (Section 1.2), and certainly in some cases appear able to produce a significant $Br^-$ content in a receiving water where it might otherwise be negligible. Since no surface water standards covering $Br^-$ have at present been promulgated, however, it is not possible to assess runoff concentrations in this light directly. Under these circumstances, it is more appropriate to examine some real life situations where motorway runoff has affected potable water supply quality and to estimate possible $Br^-$ concentrations in the light of the available data.

One such situation has arisen in the upland catchment area of the Green Withens, Booth Wood and Ringstone Edge reservoirs in Yorkshire, which lie within the Yorkshire Water Authority's South Western Division area. The catchment area of these reservoirs is traversed by the M62 Leeds-Manchester motorway, and the geographical relationship of the motorway to the reservoir is illustrated in Fig.

8.2. The reservoirs are reasonably typical in size for the area, and all receive runoff from the M62, although Green Withens receives less than the remaining two.

Due to the severe winter conditions experienced on this section of the motorway, heavy de-icing salt application is carried out during the winter months, and since the opening of the motorway in 1970, marked winter increases in $Cl^-$ levels in Booth Wood and Ringstone Edge reservoirs have been noted, and attributed to de-icing salt (Grime, unpublished). In the specific case of the winter of 1976-77, for instance, which was very severe, an estimated total of 7.22 kg $m^{-2}$ of salt was applied along the stretch of motorway concerned, compared with the total of 0.56 kg $m^{-2}$ applied to the M1 site in the present work during the winter 1980-81. During the 1976-77 period, large changes in the $Cl^-$ concentrations in the reservoirs were recorded, and accompanying $Br^-$ concentration changes for each reservoir have been calculated, assuming that the $Br^-$content of the de-icing salt used was similar to that found in this study (230 mg $kg^{-1}$, Table 5.6). In addition, an estimate of the non-salt $Br^-$contribution from runoff has been made using reservoir dilution factors derived from Grime's report (op. cit.) in conjunction with an overall flow weighted $Br^-$mean of 0.47 $mgl^{-1}$ calculated from summer $Br^-$ data in Appendix 6. The resultant figures are given in Table 8.4

TABLE 8.4: Estimated $Br^-$concentrations arising from M62 runoff in three Yorkshire reservoirs

| Reservoir | Maximum Increase in Reservoir $Cl^-$ Concn. ($mgl^{-1}$) | Salt-Associated[a] Increase in $Br^-$Concn. ($\mu gl^{-1}$) | Estimated[b] Non-Salt Runoff $Br^-$ Contribution ($\mu gl^{-1}$) | Total Increase In Reservoir $Br^-$Concn. ($\mu gl^{-1}$) |
|---|---|---|---|---|
| Booth Wood | 46 | 19.3 | 4.1 | 23.4 |
| Green Withens | 22 | 9.2 | 2.0 | 11.2 |
| Ringstone Edge | 68 | 28.6 | 6.1 | 34.7 |

a = based on de-icing salt data in Table 5.6
b = based on summer $Br^-$data (Appendix 6) and data from Grime (unpublished)

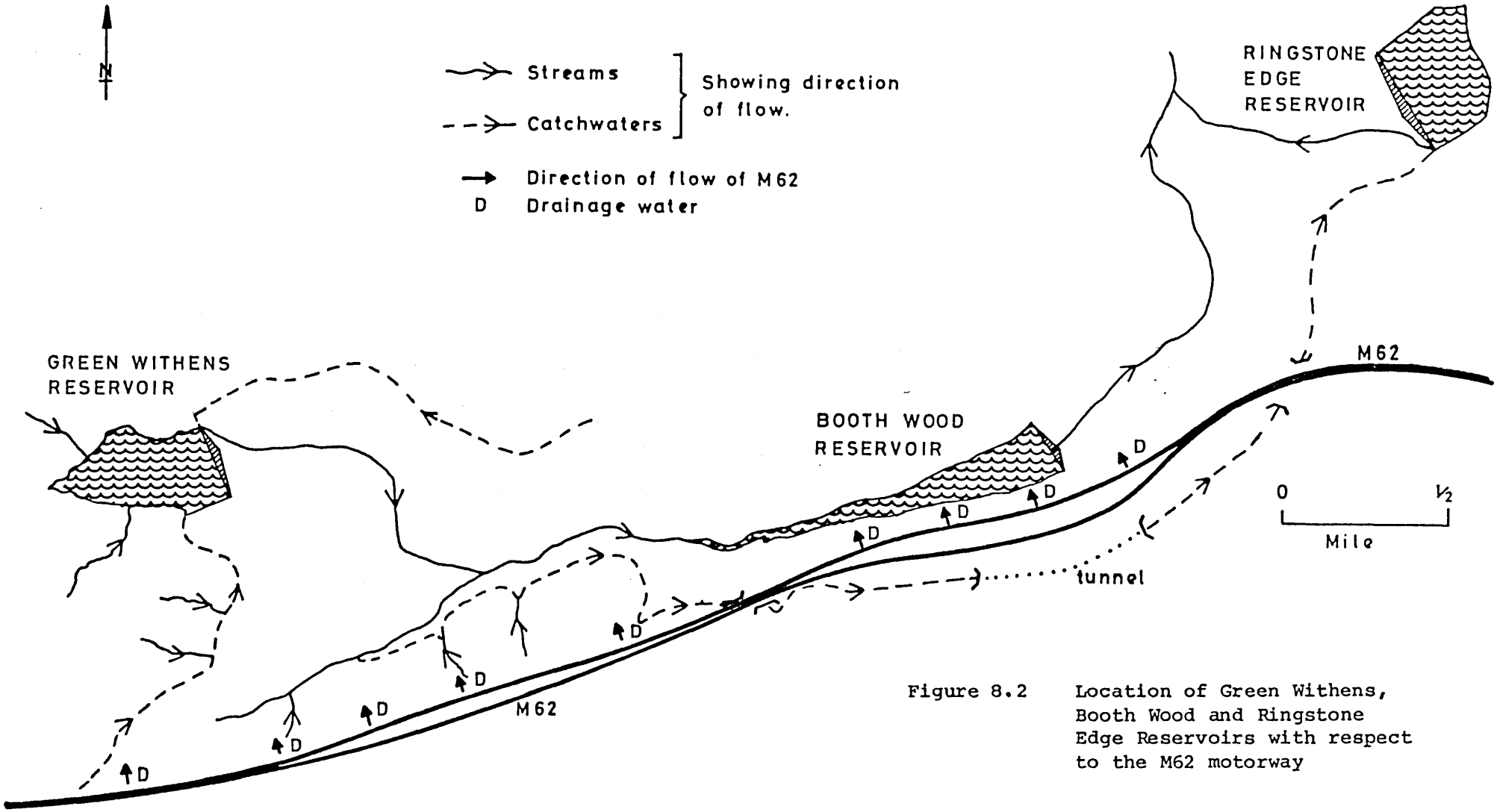



Figure 8.2 Location of Green Withens, Booth Wood and Ringstone Edge Reservoirs with respect to the M62 motorway

Although the values are very approximate, the data indicate that motorway runoff alone could lead to significant increases in $Br^-$ concentrations in these potable water sources. The salt application on this section of the M62 was, of course, very heavy during the period taken for the estimate, and for other locations and conditions the salting $Br^-$ contribution might be expected to be smaller. Since, however, the remainder of the catchment consists almost entirely of open moorland, in more urbanised catchments a denser road network, as well as other possible sources of $Br^-$, may make a contribution which is absent in the present case. It is noteworthy that, even if the reservoir waters considered contained no $Br^-$ apart from runoff contributions, the resultant concentrations in two cases are still approaching the range (50 $\mu gl^{-1}$) found by Luong et al. (1982) to produce brominated trihalomethanes during chlorination of $Br^-$-spiked upland waters.

Another location where motorway runoff has affected reservoir water quality is the Thornton reservoir near Leicester. This receives drainage from the M1 which has resulted in raised $Cl^-$ levels compared with nearby Cropston and Swithland reservoirs which do not (Rose, 1984). Comparative $Cl^-$ data for these reservoirs is given in Table 8.5 along with estimated $Br^-$ concentration increases in Thornton water. Some haloform data for treated water from Thornton and a mixture of Cropston and Swithland waters respectively are also given. Bromide data for the raw water is not available for either location.

TABLE 8.5 : Comparative $Cl^-$, $Br^-$ and haloform data from three reservoirs in Leicestershire (after Rose, 1984)

| Reservoir | Mean $Cl^-$ Concentration 1979-1983 ($mgl^{-1}$) | Estimated[a] $Cl^-$-associated $Br^-$ Concn. Increase ($\mu gl^{-1}$) | Mean Total Brominated Haloform Concn. in Treated Waters ($\mu gl^{-1}$) |
|---|---|---|---|
| Thornton | 72 | 16 | 22.4[b] |
| Cropston | 35 | - | 19.1[c] |
| Swithland | 35 | - | |

[a] = based on de-icing salt data in Table 5.6
[b] = 8 samples
[c] = 7 samples of chlorinated mixed waters

Although the influence of M1 runoff on Thornton water $Br^-$ concentrations (considering only the salting effect) is noticeable, it appears that this has not led in this particular case to a significant increase in the brominated haloform concentration, although it must be recalled that raw water $Br^-$ concentrations have been found not to be the only important factor governing brominated THM production (Luong et al., 1982). Unfortunately, the lack of raw water $Br^-$ data in the present case make it difficult to assess prevailing total $Br^-$ concentrations, but it is possible that in this particular location a combination of low background $Br^-$ levels and other factors prevent a more substantial increase in brominated THM concentrations. Nonetheless, both in this situation and the M62 example, it is clear that motorway runoff alone could cause an increase in $Br^-$ concentrations in some raw water supplies which is substantial in relation to the concentration range within which THM formation can take place. It also appears possible that supplies abstracted from lowland waters receiving runoff from urban areas in general could also receive a significant $Br^-$ contribution derived from road surface runoff. In view of this, it is perhaps not surprising some authors have recently emphasised the growing importance of $Br^-$ as a water quality parameter (Haag et al., 1984).

The clear trends evident in the analysis of factors affecting runoff loadings noted in section 5.6.3 and the use of runoff $Br^-$ data to examine $Br^-$ accumulation on the catchment both illustrate the usefulness of the well-defined and uniform site used in the present work for examining some of the basic processes affecting motorway runoff quality. This recalls the fact that reduction of the number of variables affecting runoff quality (in order to facilitate study of basic processes) was a motivating factor behind several of the studies of specific highway catchments noted in section 1.1.1. Although predictive modelling of M1 runoff quality was outside the scope of the present work, use of catchments such as the M1 site for modelling purposes would appear to be soundly based in the light of the difficulties encountered in the field of urban runoff quality modelling. In this area, a fundamental problem is that, while hydrological and hydraulic processes in urban drainage systems are relatively well understood, the underlying processes governing runoff quality are not (Shubinski and Roesner, 1983). Because of this, it is widely

recognised that runoff quality models which are constructed for a primarily practical purpose should be location-specific and based on locally-gathered data (Jewell and Adrian, 1982).

In this context, a sensible aim of this type of work in the UK with some probable practical benefits would appear to be the development of a "location-type specific" runoff pollutant loading model specifically for motorway surfaces, since, although local conditions vary widely, motorway catchments in general are still far more uniform and have more characteristics in common than almost any other type. The practical benefits of such a model might include, for example, the estimation of annual suspended solids loads which would be received by a runoff treatment system, or the assessment of the impact of motorway runoff quality in sensitive catchments. The development of such a model for US conditions was one of the aims of the Federal Highways Authority study (1981c) previously referred to (section 1.1.3). Considering the general simplicity of the approach taken, the ability of the model to predict seasonal total solids loadings to within generally less than ±30% of those estimated from field data from the five sites studied indicates a considerable potential usefulness for motorway-specific runoff modelling. Thus, although development of a generally applicable model of this type clearly requires far greater resources than were available for the present work, in terms of indicating important variables which influence parameter loadings, the data from this study could be considered a useful potential contribution towards building a UK-specific motorway runoff quality model, should sufficient data from other sites ever become available to make production of a such a model a realistic possibility. At present, work is in progress to collate and distribute relevant data from many of the highway and urban runoff studies in progress or already completed in Europe (Colyer, 1983), and it is possible that this may improve the prospects for the developments of this type. In the absence of a suitable predictive model, however, the annual loading data derived from the present work (Fig. 8.1B) provides an indicator of the magnitude of pollutant loads which may be expected from a length of heavily-used motorway.

In conclusion, it is perhaps appropriate to consider a wider aspect of the present work as a whole. Mance (1982) noted that only

one of the eight studies of UK urban runoff which he reviewed had simultaneously investigated the quality of atmospheric deposition, in order to assess the sources of the urban stormwater pollution being studied (Mance and Harman, 1978). In the present work, however, by focussing specifically on the elements Pb and Br in a well-defined catchment, discrete sources have been quite clearly identified and some detailed links established between these elements in ambient air, deposition and runoff. This has made it possible to throw more light on some aspects of the behaviour of these elements in a motorway environment as they are transferred from ambient air to surface waters. In doing so, the work has involved contact with three broad, superficially unconnected areas of environmental concern: air pollution from vehicle emissions, surface water pollution from urban runoff and trihalomethanes in potable water supplies. Consideration of sludge quantities arising from motorway runoff treatment has also touched upon the area of solid waste disposal. The interlinking of these areas through this work could therefore be seen as an appropriate reminder of the increasing awareness of the need to consider pollutant transfer between different media (Cohen and Ryan, 1985; Dowd, 1985) and it appears that this could become an area of increasing research effort in the future.

## SECTION 9. SUMMARY AND CONCLUSIONS

9.1 A review of the relevant literature indicated that road surface runoff contains substances of concern such as Pb, suspended solids, PAH and hydrocarbons at concentrations which may make an increasingly important impact on surface water quality as wastewater treatment processes are improved and water quality standards raised.

9.2 Although $Br^-$ is increasingly recognised as an important water quality parameter because of its role in THM formation, no studies concerning the possible contribution of road and urban runoff to the presence of $Br^-$ in surface waters have previously been reported.

9.3 Seasonal differences were evident in several aspects of site hydrology, and for sampled events a clear trend to higher mean flows, peak flows and shorter durations in summer was evident.

9.4 Over the entire sampling period, concentrations of many parameters in individual samples varied by up to two orders of magnitude. Most overall variation was noted for parameters affected by application of de-icing salt, which was considered to be the most significant single seasonal factor affecting runoff quality.

9.5 Detailed assessment of the impurities in de-icing salt indicated that these may contribute significantly to concentrations of TSS, $Br^-$ and possibly Cd in runoff. Contributions to Pb and Zn levels were found to be negligible.

9.6 The nature and particle size distribution of TSS in runoff was markedly affected by the presence of significant quantities of oil and associated materials, and it was evident that mixing of road surface dust with a surface oil film took place during runoff events.

9.7 The majority of Pb in runoff was solid-associated, Zn showed varying degrees of solid-association and the majority of Cd was in the dissolved state.

9.8 The oil content of runoff suspended solids was found to be fairly consistent in the region of 7%, and the associated PAH

showed a relatively uniform relationship with oil levels. Loss of lubricating oil was considered to be a major source of both oil and PAH, and estimated runoff concentrations were comparable with published values.

9.9 Tyre rubber wear products were considered to be the dominant potential source of Zn in runoff, possibly substantial for Cd but insignificant for Pb. Lubricating oil losses did not appear to make a substantial contribution to Zn loads.

9.10 In general, background deposition was not a major source of runoff contaminants at the site.

9.11 Regression analysis of runoff loads indicated that in-storm hydrological parameters were the main variables to affect TSS and Pb, while in summer $Cl^-$ loads were heavily influenced by ADPT. Zinc loads demonstrated behaviour intermediate between TSS and $Cl^-$, which was considered due to its variable degree of solid-association. No clear evidence for the effect of de-icing salt on TSS loads was found.

9.12 The results of the regression analyses demonstrated the usefulness of the M1 site for examining basic processes governing runoff quality.

9.13 Analysis for $Br^-$ and $Cl^-$ in runoff and other samples by INAA was found to be satisfactory, although sample preparation was time-consuming for runoff samples. The applicability of the method to both aqueous and solid samples was, however, considered to be a major advantage.

9.14 Bromide concentrations in runoff were found to be up to two orders of magnitude greater than reported background values. Vehicle emissions were the main source of $Br^-$ in runoff on an annual basis, while de-icing salt contributed up to 35% of the winter load.

9.15 A significant decrease in the Br/Pb ratio in deposition and road dust with respect to air values was observed, and this was attributed to Br loss by volatilisation or leaching from deposited particulates.

9.16 In contrast to Pb, $Br^-$ was solubilised relatively rapidly during individual events and thus more effectively removed from the road surface. This led to Br/Pb ratios in runoff often much higher than in air or deposition.

9.17 Regression analysis showed $Br^-$ loads to be significantly influenced by ADPT, and a $Br^-$ deposition rate derived from runoff data was in good agreement with measured values. Accumulation of $Br^-$ on the road surface was considered possibly due to a surface adsorption mechanism.

9.18 Treatment of motorway runoff by a french drain was found to be more efficient at solids removal than a sedimentation tank. Removal efficiencies for both systems were found to be better in summer, which was considered partially due to efficient removal of the larger solids mobilised by summer events.

9.19 Comparison of annual unit area loading values for several parameters from the motorway site with published values for urban runoff indicated the dominant contribution of road surfaces to urban stormwater pollution. Runoff concentrations were frequently in excess of effluent and surface water standards. For $Br^-$, estimated surface water concentrations arising from motorway runoff at some points of potable supply abstraction in the UK approached values reported to lead to brominated THM formation during chlorination.

REFERENCES

Abdullah, M.I. and Royle, L.G. (1973). The occurrence of lead in natural waters. Proc. Int. Symp. on Environmental Health Aspects of Lead. Commission of the European Communities, Luxembourg, 113.

Adams, W.R. (1981). Interstate highways versus watershed protection in New England. J. Am. Water Works Assoc., 73, 346.

Ahmed, R. and Schiller, R. (1980). Non-point source quantification and its role in lake and stream water quality planning. Prog. Wat. Tech., 13, 783.

Alley, W.M. and Smith, P.E. (1981). Estimation of accumulation parameters for urban runoff quality modelling. Wat. Resources. Res., 17, 1657.

American Chemical Society (1978). Cleaning our environment; a chemical perspective. Report by the Committee on Environmental Improvement. American Chemical Society, Washington DC.

American Society for Testing and Materials (1977). Annual Book of ASTM Standards, 31, 356.

Amiel, S. (1981). Non-destructive Activation Analysis. Wiley Interscience, New York, USA.

Anon (1984). New research in progress. Public Roads, 48, 139.

Asplund, R., Mar, B.W. and Ferguson J.F. (1982). Total suspended solids in highway runoff in Washington State. J. Environ. Eng. Div., Am. Soc. Civ. Eng., 108, 391.

Associated Octel (1981). Associated Octel Company Ltd., Bletchley, UK, Personal Communication.

Bachus, W.O. (1975). Water management - are we on the right track? Proc. Int. Seminar and Exposition on Water Resources Instrumentation, Chicago, 1974. Ann Arbor Science Publishers, Ann Arbor, Mich., USA, xxix.

Balades, J.D., Cathelain, M., Marchandise, P., Peybernard, J. and Pilloy, J.C. (1984). Chronic pollution of intercity motorway runoff waters. Wat. Sci. Tech., 17, 1165.

Bartlett, R.E. (1981). Surface Water Sewerage, 2nd Edition, Applied Science Publishers Ltd., London, UK.

Baumann, H. and Heumann, K.G. (1985). Brom/blei-verhältnisse in aerosolen und autoabgasen. Fresenius. Z. Anal. Chem., 320, 512.

Bellinger, E.G., Jones, A.D. and Tinker, J. (1982). The character and dispersal of motorway runoff water. Wat. Pollut. Control, 81, 372.

Biggins, P.D.E. and Harrison, R.M. (1979). Atmospheric chemistry of automotive lead. Environ. Sci. Technol., 13, 558.

Biggins, P.D.E. and Harrison, R.M. (1980). Chemical speciation of lead compounds in street dusts. Environ. Sci. Technol., 14, 336.

Boggess, W.R. and Wixson, B.G. (1979). Lead in the Environment. Castle House Publications Ltd.

Borch-Jensen, J.E. (1978). Runoff from motorways passing open country or rural areas. Proc. OECD Symp. on Road Drainage, Berne, Switzerland. OECD, Paris, 364.

Bosset, E. (1978). Pollution de terrains aquifères par hydrocarbures: prévention et assainissement. Proc. OECD Symp. on Road Drainage, Berne, Switzerland. OECD, Paris 418.

Bowen, H.J.M. (1979). Environmental Chemistry of the Elements. Academic Press, London.

Boyer, K.W. and Laitinen, H.A. (1974). Lead halide aerosols - some properties of environmental significance. Environ. Sci. Technol., 8, 1093.

British Crop Protection Council (1979). The Pesticide Manual, Worthing, C.R. (ed.), British Crop Protection Council, Croydon, UK.

British Standards Institution (1965). British Standards Specification 3680 (part 4A), Thin plate weirs and venturi flumes. British Standards Institution, London, UK.

Bufill, M. (1981). Hydrological aspects of the study of non-point pollution on a motorway catchment. MSc Thesis, Imperial College, London.

Bull, R.J. (1982). Health effects of drinking water disinfectants and disinfectant by-products. Environ. Sci. Technol., 16, 554A.

Bullin, J.A., Bower, S.C., Hinz, M. and Moe, R.D. (1985). Aerosols near urban street intersections. J. Air Pollut. Control Assoc., 35, 355.

Bullin, J.A. and Moe, R.D. (1982). Measurement and anaylsis of aerosols along Texas roadways. Environ. Sci. Technol., 16, 197.

Butters, R. (1985). Toddington Motorway Maintenance Depot, Beds., UK, Personal Communication.

Cadle, S.H. and Williams, R.L. (1978). Gas and particle emissions from automobile tyres in laboratory and field studies. J. Air. Pollut. Control. Assoc., 28, 502.

Carter, K.B. (1985). Protecting our investment in clean water. J. Water Pollut Control Fed., 57, 104.

Cathelain, M., Friant, G. and Olie, J.-L. (1981). Les eaux de ruissellement de chaussées autoroutières: évaluation des charges de pollution. Bull. de Liaison Laboratoire des Ponts et Chaussées, No. 116, 9.

Cawse, P.A. (1980). Deposition of trace elements from the atmosphere in the UK. In Inorganic Pollution and Agriculture. Ministry of Agriculture, Fisheries and Food Reference Book 326, HMSO, London, 22.

Cawse, P.A. (1981). A survey of atmospheric trace elements in the UK: results for 1979. UKAEA Report No. R9886, HMSO, London.

Cawse, P.A. and Pierson, DH. (1972). An analytical study of trace elements in the atmospheric environment. UKAEA Report No. 7134, HMSO, London.

Chollar, B.H. (1974). Federal Highway Administration research on calcium magnesium acetate - an alternative de-icer. Public Roads, 47, 113.

Christensen, E.R. and Guinn, V.P. (1979). Zinc from automobile tyres in urban runoff. J. Environ. Eng. Div., Am. Soc. Civ. Eng., 105, 165.

Chui, T.W., Mar, B.W. and Horner, R.R.(1982). Pollutant loading model for highway runoff. J. Environ. Eng. Div., Am. Soc. Civ. Eng., 108, 1193.

Clark, A.I., McIntyre, A.E., Lester, J.N. and Perry, R. (1984). Ambient air measurements of aromatic and halogenated hydrocarbons at urban, rural and motorway locations. Sci. Total Environ., 39, 265.

Clemente, G.F. and Mastinu, G.G. (1974). Instrumental method for the determination of trace elements in water samples by neutron activation analysis. J. Radioanal. Chem., 20, 707.

Cohen, Y. and Ryan, P.A. (1985). Multimedia modelling of environmental transport: trichlorethylene test case. Environ. Sci. Technol., 19, 412.

Collins, P.G. and Ridgway, J.W. (1980). Urban storm runoff quality in S.E. Michigan, J. Environ. Eng. Div., Am. Soc. Civ. Eng., 106, 153.

Colwill, D.M. (1985). Transport and Road Research Laboratory, Crowthorne, Berks, UK, Personal Communication.

Colwill, D.M. and Hickman, A.J. (1981). Measurement of particulate lead on the M4 at Harlington, Middlesex. Third Report. Transport and Road Research Laboratory Report 972, TRRL, Crowthorne, Berks, UK.

Colwill, D.M., Peters, C.J. and Perry, R. (1984). Water quality of motorway runoff. Transport and Road Research Laboratory Supplementary Report 823, TRRL, Crowthorne, Berks, UK.

Colyer, P.J. (Ed.) (1983). European Research Information Exchange on Urban Hydrology/Hydraulics. Hydraulics Research Station, Wallingford, Oxon., UK.

Cooper, W.J., Zika, R.G. and Steinhauer, M.S. (1985). Bromide-oxidant interactions and THM formation: a literature review. J. Am. Water Works Assoc., 77, 116.

Council of the European Communities (1975). Council directive of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the member states, Directive 75/440/EEC. Off. J. Eur. Comm., L194, 26.

Crecelius, E.A., Lepel, E.A., Laul, J.C., Rancitelli, L.A. and McKeever, R.L. (1980). Background air particulate chemistry near Colstrip, Montana. Environ. Sci. Technol., 14, 422.

Crowley, S. (1981). The environmental impact of de-icing salts used on roads - a literature review. MSc Thesis, Imperial College, London, UK.

Dams, R., Robbins, J.A., Rahn, K.A. and Winchester, J.W. (1970). Non-destructive neutron activation analysis of air pollution particulates. Anal. Chem., 42, 861.

Dannis, M.L. (1974). Rubber dust from the normal wear of tyres. Rubber Chem. Technol., 47, 1011.

Davies, O.L. and Goldsmith, P.L. (1977). Statistical Methods in Research and Production, 4th Edition. Longman Ltd., London, UK.

Dauber, L., Novak, B., Zobrist, J. and Zürcher, F. (1978). Pollutants in motorway stormwater runoff. Proc. OECD Symp. on Road Drainage, Berne, Switzerland, OECD, Paris, 332.

Demayo, A., Taylor, M.C., Taylor, K.W. and Hodson, P.V. (1982). Toxic effects of lead and lead compounds on human health, aquatic life, wildlife plants and livestock. CRC Crit. Rev. Environ. Control, 12, 257.

Department of the Environment (1972). The Analysis of Raw, Potable and Waste Waters. HMSO, London, UK.

Department of the Environment (1976). Specification of Road and Bridge Works. HMSO, London, UK.

Dove, K. (1982). Bedfordshire County Council, Personal Communication.

Dussart, G.B.J. (1984). Effects of motorway runoff on the ecology of stream algae. Water Pollut. Control, 83, 409.

Dzubay, T.G. and Stevens, R.K. and Richards, L.W. (1979). Composition of aerosols over Los Angeles freeways. Atmos. Environ., 13, 653.

Ellis, J.B. (1977). The characterisation of particulate solids and quality of water discharged from an urban catchment. In Effects of Urbanisation and Industrialisation on the Hydrological Regime and Water Quality. Proc. IAHS/UNESCO Amsterdam Symp., IAHS/UNESCO, Paris, 283.

Ellis, J.B. (1979). The nature and sources of urban sediments and their relationship to water quality: a case study from N.W. London. In Man's Impact on the Hydrological Cycle in the UK. Hollis, G.E. (ed.), Geo Abstracts Ltd., Norwich, UK, 199.

Ellis, J.B., Hamilton, R. and Roberts, A.H. (1981). Composition of suspended solids in urban stormwater. Proc. 2nd Int. Conf. on Urban Storm Drainage, Urbana, Illinois, Yen, B.C. (ed.), 184.

Ellis, J.B. and Harrop, D.O. (1984). Variations in solids loadings to roadside gully pots. Sci. Total Environ., 33, 203.

Ellis, J.B. and Revitt, D.M. (1982). Incidence of heavy metals in street surface sediments: solubility and grain size studies. Water, Air Soil Pollut., 17, 82.

Ellis, J.C. and Lacey, R.F. (1980). Sampling: defining the task and planning the scheme. Water Pollut. Control, 79, 452.

Ellis, K.M. and Chattopadhyay, A. (1979). Multielement determination in estuarine suspended particulate matter by instrumental neutron activation analysis. Anal. Chem., 51, 942.

Farmer, J.G. and Cross, J.D. (1978). Bromine in soil - an indicator of automobile exhaust lead pollution? Water, Air Soil Pollut., 9, 193.

Federal Highway Administration (1981a). Constituents of highway runoff, Vol. IV, Characteristics of runoff from operating highways. Research Report FHWA-RD-81/045, Washington, DC.

Federal Highway Administration (1981b). Constituents of highway runoff, Vol I, State-of-the-art report. Research Report FHWA-FD-81/042, Washington, DC.

Federal Highway Administration (1981c). Constituents of highway runoff, Vol III, Predictive procedure for determining pollutant characteristics in highway runoff. Research Report FHWA-FD-81/044, Washington, DC.

Feick, G., Horne, R.A. and Yeaple, D. (1972). Release of mercury from contaminated freshwater sediments by the runoff of road deicing salt. Science, 175, 1142.

Field, R., Struzeski, E.J., Masters, H.E. and Tafuri, A.N. (1974). Water pollution and associated effects from street salting. J. Environ. Eng. Div., Am. Soc. Civ. Eng., 100, 459.

Filby, R.H. and Shah, K.R. (1975). Neutron activation methods for trace elements in crude oils. In The Role of Trace Metals in Petroleum, Yen, T.F. (ed.), Ann Arbor Science Publishers, Mich., USA, 89.

Floss, R. and Sauer, G. (1978). Surface runoff and protection of highway environments. Proc. OECD Symp. on Road Drainage, Berne, Switzerland, OECD, Paris, 343.

Foley, P.D. and Massingham, G.A. (1976). Monitoring of community water supplies. J. Am. Water Works Assoc., 68, 105.

Förstner, U. and Wittman, G.T.W. (1981). Metal Pollution in the Aquatic Environment, 2nd Edition, Springer-Verlag, New York.

Gardner, M.J. (1982). Adsorption of trace metals from solution during filtration of water samples. Water Research Centre Technical Report TR172, WRC, UK.

Ganley, J.T. and Springer, G.S. (1974). Physical and chemical characteristics of particulates in spark ignition engine exhausts. Environ. Sci. Technol., 8, 340.

Giauque, R.D., Goda, L.Y. and Brown, N.E. (1974). Characterisation of aerosol in California by X-ray induced X-ray fluorescence analysis. Environ. Sci. Technol., 8, 436.

Gjessing, E., Lygren, E., Berlind, L., Gulbrandsen, T. and Skaane, R. (1984). Effect of highway runoff on lake water quality. Sci. Total. Environ., 33, 245.

Goettle, A. and Krauth, K. (1980). Total pollution loads considering urban storm runoff. Prog. Wat. Tech., 13, 155.

Graham, N.J.D. (1977). An investigation of sediment transport and associated contaminants from motorway runoff. MSc Thesis, Imperial College, London, UK.

Green, E.H. (1974). Black deposits on motorways. Transport and Road Research Laboratory Supplementary Report 74UC, TRRL, Crowthorne, Berks, UK.

Grime, M.B. (Unpublished). The effect of road de-icing salts on a potable water catchment. Yorkshire Water Authority, South Western Division.

Haag, W.R., Hoigné, J. and Bader, H. (1984). Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment. Water Res., 18, 1125.

Habib, S. and Minski, M.J. (1981). Neutron activation analysis techniques for the analysis of the soluble and particulate fractions of river water. J. Radioanal. Chem., 63, 379.

Habibi, K. (1973). Characterisation of particulate matter in vehicle exhaust. Environ. Sci. Technol., 7, 223.

Hahne, H.C.H. and Kroontje, W. (1973). Significance of pH and chloride concentration on behaviour of heavy metal pollutants: mercury (II), cadmium (II), zinc (II) and lead (II). J. Environ. Quality, 2, 444.

Hamilton, R.S., Revitt, D.M. and Warren R.S. (1984). Levels and physico-chemical associations of Cd, Cu, Pb and Zn in road sediments. Sci. Tot. Environ., 33, 59.

Harkov, R. and Greenberg, A. (1985). Benzo(a)pyrene in New Jersey - results from a twenty-seven-site study. J. Air Pollut. Control Assoc., 35, 238.

Haroz, R. (1983). The toxicology of polycyclic organic matter from exhaust gases. In Mobile Source Emissions Including Polycyclic Organic Species, Rondia, D., Cooke, M. and Haroz, R.K. (eds.), Reidel, Dordrecht, The Netherlands, 77.

Harrison, R.M. (1979). Toxic metals in street and household dusts. Sci. Tot. Environ., 11, 89.

Harrison, R.M., Laxen, D.P.H. and Wilson, D.P.H. (1981). Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils. Environ. Sci. Technol., 15, 1378.

Harrison, R.M., Perry, R. and Wellings, R.A. (1975). Polynuclear aromatic hydrocarbons in raw, potable and wastewaters. Water Res., 9, 331.

Harrison, R.M. and Sturges, W.T. (1983a). The measurement and interpretation of Br/Pb ratios in airborne particles. Atmos. Environ., 17, 311.

Harrison, R.M. and Sturges, W.T. (1983b). Bromine to lead ratios in atmospheric particles at urban and rural sites. Proc. Int. Conf. on Heavy Metals in the Environment, Heidelberg, W. Germany, CEP Consultants, Edinburgh, 132.

Harrison, R.M. and Williams, C.R. (1982). Airborne cadmium, lead and zinc at rural and urban sites in north west England. Atmos. Environ., 16, 2669.

Harrison, R.M. and Wilson, S.J. (1985a). The chemical composition of highway drainage waters I. Major ions and selected trace metals. Sci. Tot. Environ., 43, 79.

Harrison, R.M. and Wilson, S.J. (1985b). The chemical composition of highway drainage waters II. Chemical associations of metals in the suspended sediment. Sci. Tot. Environ., 43, 79.

Harrison, R.M. and Wilson, S.J. (1985c). The chemical composition of highway drainage waters III. Runoff water metal speciation characteristics. Sci. Tot. Environ., 43, 79.

Harrison, S.H., La Fleur, P.D. and Zoller, W.H. (1975). Evaluation of lyophilization for the pre-concentration of natural water samples prior to neutron activation analysis. Anal. Chem., 47, 1685.

Harrop, O. (1983). Stormwater pollution from highway surfaces: a review. Research Report 6, Midsdlesex Polytechnic Research Report Series.

Harsch, D.E. and Rasmussen, R.A. (1977). Identification of methyl bromide in urban air. Anal. Lett., 10, 1041.

Hawkins, R.G.P. (1983). Legislation and enforcement. In Disposal and Recovery of Municipal Solid Waste, Henstock, M.E. (ed.), Butterworths, London, UK.

Hedley, G. and Lockley, J.C. (1975). Quality of water discharged from an urban motorway. Water Pollut. Control, 74, 659.

Hieirli, R. (1978). Construction des séparateurs d'huile et des écrans d'étanchiéité. Proc. OECD Symp. on Road Drainage, Berne, Switzerland, OCED Paris, 401.

Hirschler, D.A., Gilbert, L.F., Lamb, F.W. and Niebylski, L.M. (1957). Particulate lead compounds in automobile exhaust gas. J. Ind. Eng. Chem., 49, 1131.

Hoffman, E.J., Mills, G.L., Latimer, J.S. and Quinn, J.G. (1984). Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. Environ. Sci. Technol., 18, 580.

Hollowell, C.D., Dod, R.L., Giauque, R.D., Traynor, G.W. and Novakov, T. (1977). Characterisation of winter air pollution episodes. Atmos. Aerosol Res. Ann. Report, 1976-1977, Lawrence Berkeley Laboratory Report LBL-6819, 92.

Hopke, P.K., Lamb, R.E. and Natusch, D.F.S. (1980). Multielemental characterisation of urban roadway dust. Environ. Sci. Technol., 14, 164.

Huntzicker, J.J., Friedlander, S.K. and Davidson, C.I. (1975). Material balance for automobile-emitted lead in Los Angeles basin. Environ. Sci. Technol., 9, 448.

Imperial Chemical Industries plc (1983). Mond Division, Cheshire, UK, Personal Communication.

Irving Sax, N. (1979). Dangerous Properties of Industrial Materials (5th Edition), Van Nostrand, New York.

Jewell, T.K. and Adrian, D.D. (1982). Statistical analysis to derive improved stormwater quality models. J. Water Pollut. Control Fed., 54, 489.

Johnston, W.R. and Harrison, R.M. (1984). Deposition of metallic and organic pollutants alongside the M6 motorway. Sci. Total Environ., 33, 119.

Khandekar, R.N., Kelkaar, D.N. and Vohra, K.G. (1982). Bromine to lead ratios in suspended air particulate matter in Greater Bombay. Atmos. Environ., 16, 621.

Klein, H. (1982). Die Beschaffenheit der Neiderschlagsabflüsse von Autobahnen. Wasserwirtschaft, 72, 37.

Kleopfer, R.D. and Fairless, B.J. (1972). Characterisation of organic components in muncipal water supply. Environ. Sci. Technol., 6, 1036.

Kolthoff, I.M. and Yutzy, H. (1937). Volumetric determination of bromide after oxidation to bromate in the presence of much chloride. Ind. Eng. Chem. (Anal. Edn.), 9, 75.

Kool, H.J., van Kriejl, C.F. and Zoetman, B.C.J. (1982). Toxicology assessment of organic compounds in drinking water. CRC Crit. Rev. Environ. Control, 12, 307.

Kowalczyk, G.S., Gordon G.E. and Rheingrover, S.W. (1982). Identification of atmospheric particulate sources in Washington, DC, using chemical element balances. Environ. Sci. Technol., 16, 79.

Krishnamurty, K.V., Shpirt, E. and Reddy, M.M. (1976). Trace metal extraction of soils and sediments by nitric acid-hydrogen peroxide. At. Abs. Newsletter, 15, 68.

Kruger, P. (1971). Principles of Activation Analysis. Wiley Interscience, New York, USA.

Lagerwerff, J.V. and Specht, A.W. (1970). Contamination of roadside soils with cadmium, nickel, lead and zinc. Environ. Sci. Technol., 4, 583.

Laxen, D.P.H. and Harrison, R.M. (1977). The highway as a source of water pollution: an appraisal with the heavy metal lead. Water Res., 11, 1.

Leinster, P., Perry, R. and Young, R.J. (1978) Ethylene dibromide in urban air. Atmos. Environ., 12, 2383.

Li, T.M. and Smith, C.C. (1976). Emissions of sulphuric acid and the nature of halide emitted from a car. Internal report, Associated Octel Ltd., Bletchley, UK.

Lieser, K.H. and Neitzert, V. (1976). Determination of trace elements in water by non-destructive neutron activation. J. Radioanal. Chem., 31, 397.

Little, P. and Wiffen, R.D. (1978). Emission and deposition of lead from motor exhausts - II. Airborne concentration, particle size and deposition of lead near motorways. Atmos. Environ., 12, 1331.

Loucks, R.H. and Winchester, J.W. (1970) Pollution contributions to the atmospheric inventory of chlorine and bromine in aerosols over continental USA. In Trace Substances in Environmental Health - III, Hemphill, D.D. (ed.), University of Missouri, USA, 233.

Luong, T.V. (1983). Halogenated organic materials in water supplies. PhD Thesis, Imperial College, London, UK.

Luong, T.V., Peters, C.J. and Perry, R. (1982). Influence of bromide and ammonia upon the formation of trihalomethanes under water treatment conditions. Environ. Sci. Technol., 16, 473.

Luong, T.V., Peters, C.J. and Perry, R. (1983). Occurrence of bromide in source and treated waters. Effl. Water Treat. J., 23, 192.

Luong, T.V., Peters, C.J., Young, R.J. and Perry, R. (1980). Bromide and trihalomethanes in water supplies. Environ. Technol. Lett., 1, 299.

Luten, J.B., Das, H.A. and De Ligny, C.L. (1977). The determination of bromine and iodine in environmental water samples by thermal neutron activation and isotope exchange. J. Radioanal. Chem., 35, 147.

Lyong, W.S. (1964). Guide to Activation Analysis. Van Nostrand, Princeton, New Jersey, USA.

McIntyre, A.E., Perry, R. and Lester, J.N. (1981). Analysis of polynuclear aromatic hydrocarbons in sewage sludges. Anal. Lett., 14, 18.

McKee, J.S.C., Lapointe, C. and Wise, M.L.H. (1980). An analysis of lead, bromine, zinc and sulphur in airborne particulate matter by X-ray fluorescence spectrosocpy. J. Environ. Sci. Health, A(15), 1.

Mance, G. (1982). Factors affecting the quality of urban storm discharges in the UK. Proc. 1st Int. Seminar on Urban Drainage Systems, Southampton. Featherstone, R.E. and James, A. (eds), Pitmans Press, London, UK, 3-17.

Mance, G. and Harman, M.M.I. (1978). The quality of urban stormwater runoff. Proc. Int. Conf. on Urban Storm Drainage, Southampton. Helliwell, P.R. (ed.), Pentech Press, London, UK, 603.

Maoza, A.A. (1979). An investigation of hydrocarbon pollution in soils close to a motorway. MSc Thesis, Imperial College, London, UK.

Martens, C.S., Wesolowski, J.J., Kaifer, R. and John, W. (1973). Lead and bromine particle size distributions in the San Francisco Bay area. Atmos. Environ., 7, 905.

Masschelein, W.J. and Denis, M. (1981). The specific determination of bromide in natural waters. Water Res., 15, 857.

Meteorological Office (1980). MON 1 Service data, Station no. 24001, Meteorological Office, Bracknell, Berks, UK.

Minski, M.J. (1980). University of London Reactor Centre, Ascot, Berks, UK, Personal Communication.

Mochida, K. and Yamasaki, M. (1984). Toxicity of halomethanes to cultured human and monkey cells. Bull. Environ. Contam. Toxicol., 33, 253.

Morrison, G.M.P., Revitt, D.M., Ellis, J.C., Svensson, G. and Balmer, P. (1984). The physico-chemical speciation of zinc, cadmium, lead and copper in urban stormwater. Proc. 3rd Int. Conf. on

Urban Storm Drainage, Göteborg, Sweden, Vol. 3. Balmer, P., Malmquist, P-A, and Sjöberg, A. (eds.), 989.

Moyers, J.L., Zoller, W.H., Duce, R.A. and Hoffman, G.L. (1972). Gaseous bromine and particulate lead, vanadium and bromine in a polluted atmosphere. Environ. Sci. Technol., 6, 68.

Munger, J.W. and Eisenreich, S.J. (1982). Continental-scale variations in precipitation chemistry. Environ. Sci. Technol., 17, 32A.

Nadkarni, R.A. and Morrison, G.H. (1978). Multielement analysis of lake sediments by neutron activation analysis. Anal. Chim. Acta., 99, 133.

Nikolaou, K., Masclet, P. and Mouvier, G. (1984). Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere - a critical review. Sci. Total Environ., 32, 103.

O'Connor, B.H., Kerrigan, G.C. and Nouwland, C.R. (1978). Temporal variation in atmospheric particulate lead and bromine levels for Perth, Western Australia. Atmos. Environ., 12, 1907.

O'Connor, B.H., Kerrigan, G.C., Thomas, W.W. and Pearce, A.T. (1977). Use of bromine levels in airborne particulate samples to infer vehicular lead concentrations in the atmosphere. Atmos. Environ., 11, 635.

Ofori, D.K. (1984a). Removal of contaminants from road surface runoff. PhD Thesis, Imperial College, London, UK.

Ofori, D.K. (1984b). Imperial College, London, UK. Personal Communication.

Olson, K.W. and Skogerboe, R.K. (1975). Identification of soil lead compounds from automotive sources. Environ. Sci. Technol., 9, 227.

Ondov, J.M., Zoller, W.H. and Gordon, G.E. (1982). Trace element emissions on aerosols from motor vehicles. Environ. Sci. Technol., 16, 318.

Paciga, J.J., Roberts, T.M. and Jervis, R.E. (1975). Particle size distributions of lead, bromine and chlorine in urban-industrial aerosols. Environ. Sci. Technol., 9, 1141.

Patty, F.A. (1963). Industrial Hygiene and Toxicology, Vol. II, Interscience, New York, USA.

Peters, C.J. (1985). Greater London Council, Personal Communication.

Peters, C.J. and Perry, R. (1983). Treatment of Motorway Runoff. Unpublished Report for Transport and Road Research Laboratory, Crowthorne, Berks, UK.

Pierrard, J.M. (1969). Photochemical decomposition of lead halides from automobile exhaust. Environ. Sci. Technol., 3, 48.

Pierson, W.R. and Brachaczek, W.W. (1974). Airborne particulate debris from rubber tyres. Rubber Chem. Technol., 47, 1275.

Pierson, W.R. and Brachaczek, W.W. (1976). Particulate matter associated with vehicles on the road. Soc. Automotive Eng. Trans., 85, 209.

Pitt, R. (1979). Demonstration of non point pollution abatement through improved street cleaning practices. US Environmental Protection Agency Report No. EPA-60/2-79-161.

Pope, W. (1979a). Unpublished Report for Transport and Road Research Laboratory, Crowthorne, Berks, UK.

Pope, W. (1979b). Imperial College, London, UK, Personal Communication.

Pope, W. (1980). Impact of man in catchments (ii) Roads and urbanisation. In Water Quality in Catchment Ecosystems, Gower, A. (ed.), Wiley, London, 73.

Pope, W., Young, R.J. and Perry, R. (1978a). Correlations of hydrological conditions with water quality in motorway runoff. Proc. OECD Symp. on Road Drainage, Berne, Switzerland, OECD, Paris 384.

Pope, W., Graham, N.J.D., Young, R.J. and Perry, R. (1978b). Urban runoff from a road surface - a water quality study. Prog. Wat. Tech., 10, 533.

Pope, W., Young, R.J., Sollars, C.J. and Perry, R. (1979). The distribution of selected heavy metals in a motorway environment. Proc. Int. Conf. on Heavy Metals in the Environment, London, CEP Consultants, Edinburgh, 230.

Pratt, C.J. and Adams, J.R.W. (1984). Sediment supply and transmission via roadside gully pots. Sci. Total Environ., 33, 213.

Prest, J. (1982). Sources of trihalomethanes and other $C_1$ and $C_2$ halo-organics in potable water. Effl. Water Treat. J., 22, 449.

Pyen, G.S., Fishman, M.J. and Hedley, A.G. (1980). Automated spectrophotometric determination of trace amounts of bromide in water. Analyst, 105, 657.

Randall, C.W. and Grizzard, T.J. (1983). Runoff Pollution. In Stormwater Management in Urbanizing Areas. Whipple, W., Grigg, N.S., Grizzard, T., Randall, C.W., Shubinski, R.P. and Tucker, L.S. (authors), Prentice Hall, New Jersey, USA, 57.

Raybold, R.L. and Byerly, R. (1972). Investigation of products of tyre wear. National Bureau of Standards Report, NBS10834, NBS, Maryland, USA.

Rentshler, W. and Schreiber, H. (1977). The temporal and local variations of lead and bromine contents. Proc. 4th Int. Clean Air Congress, Tokyo, Japan, 562.

Rook, J.J. (1974). Formation of haloforms during chlorination of natural waters. Water Treat. Exam., 23, 234.

Rook, J.J., Gras, A.A., van der Heijden, B.G., de Wee, J. (1978). Bromide oxidation and organic substitution in water treatment. J. Environ. Sci. Health, A13, 91.

Rose, P.L. (1984). Severn Trent Water Authority, Birmingham, UK, Personal Communication.

Ryan, T.A., Joiner, B.L. and Ryan, B.F. (1978). Minitab II Reference Manual. Pennsylvania State University, USA.

Salbu, B., Steinnes, E. and Pappas, A.C. (1975). Multielement neutron activation analysis of freshwater using Ge(Li) gamma spectrometry. Anal. Chem., 47, 1011.

Salomons, W. and Förstner, U. (1980). Trace metal analysis on polluted sediments. Part II: Evaluation of environmental impact. Environ. Technol. Lett., 1, 506.

Sartor, J.D. and Boyd, G.B. (1972). Water pollution aspects of street surface contaminants. US Environmental Protection Agency Report No. EPA-R2-72-081.

Seddon, A. (1975). Remarks in discussion at end of Hedley and Lockley (1975), q.v.

Shaheen, D.G. (1975). Contribution of urban roadway usage to water pollution. US Protection Agency Report No. EPA-600/2-75-00.

Shaw, P.G., McKown, D. and Manahan, S.E. (1981). Trace element determinations in shale oil products by neutron activation. Anal. Chim. Acta., 123, 65.

Shubinski, R.P. and Roesner, L.A. (1983). Stormwater models. In Stormwater Management in Urbanizing Areas, Whipple, W., Grigg, N.S., Grizzard, T., Randall, C.W., Shubinski, R.P. and Tucker, L.S. (authors), Prentice Hall, New Jersey, USA, 95.

Slanina, J., Möls, J.J., Baard, J.H., Van der Sloot, H.A. and Van Raaphorst, J.G. (1979). Collection and analysis of rainwater; experimental problems and the interpretation of results. Int. J. Environ. Anal. Chem., 7, 161.

Smith, A.M. (1982). Department of Transport, Personal Communication.

Söderlund, G. and Lehtinen, H. (1972). Comparison of discharges from urban stormwater runoff, mixed storm overflow and treated sewage. Proc. 6th Int. Conf. on Advances in Water Pollution Research, Jerusalem, Jenkins, S.H. (ed.), Pergamon, Oxford, UK.

Sollars, C.J., Peters, C.J. and Perry, R. (1982). Bromide in urban runoff - water quality considerations. In Effects of Waste Disposal on Groundwater and Surface Water. Proc. Exeter Symp., IAHS Publ. No. 139.

Sonzogni, W.C., Chesters, G., Coote, D.R., Jeffs, D.N., Konrad, J.C., Ostry, R.C. and Robinson, J.C. (1980). Pollution from land runoff. Environ. Sci. Technol., 14, 148.

Spalding, R. (1970). Selection of materials for sub-surface drains. Road Research Laboratory Report LR346, RRL, Crowthorne, Berks, UK.

Stenstrom, M.K., Silverman, G.S. and Bursztynsky, T.A. (1984). Oil and grease in urban stormwaters. J. Env. Eng. Div., Am. Soc. Civ. Eng., 110, 58.

Sterritt, R.M. and Lester, J.N. (1980). Atomic absorption spectrophotometric analysis of the metal content of waste water samples. Environ. Technol. Letts., 1, 402.

Symons, J.A., Bellar, T.A., Carswell, J.K., De Marco, J. Kropp, K.L., Robeck, G.G., Seeger, D.R., Slocum, C.J., Smith, B.L. and Stevens, A.A. (1975). National organics reconnaissance survey for halogenated organics. J. Am. Water Works Assoc., 67, 634.

Tebbutt, T.H.Y. (1983). Principles of water Quality Control, 3rd Edition, Pergamon Press, Oxford, UK.

Ter Haar, G.L. and Bayard, M.A. (1971). Composition of airborne lead particles. Nature, 22, 553.

Ter Haar, G.L., Lenane, D.L., Hu, J.N. and Brandt, M. (1972). Composition size and control of automotive exhaust particulates. J. Air Pollut. Control Assoc., 22, 39.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., 51, 844.

Van Hassel, J.H., Ney, J.J. and Garling, D.L. (1980). Heavy metals in a stream ecosystem at sites near highways. Trans. Am. Fish. Soc., 109, 636.

Vinogradov, A.P. (1959). The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd Edition. Consultants Bureau, Inc., New York, USA, and Chapman and Hall, Ltd., London, UK.

Wada, Y. and Miura, H. (1984). Quantification of accumulated loads on road surfaces and their runoff characteristics. Wat. Sci. Tech., 16, 463.

Water Research Centre (1977). Pollution from urban runoff. Notes on Water Research, No. 12, Water Research Centre, Stevenage.

Watkins, L.H. (1981). Environmental Impact of Roads and Traffic. Applied Science Publishers, London, UK.

Whipple, W. and Hunter, J.V. (1977). Non-point sources and planning for water pollution control. J. Water Pollut. Control Fed., 49, 15.

Whipple, W. and Hunter, J.V. (1981). Settleability of urban runoff pollution. J. Water Pollut. Control Fed., 53, 1726.

Williamson, P.J. (1968). Are bituminous roads damaged by salt? Road Research Laboratory Report LR148, RRL, Crowthorne, Berks, UK.

Winchester, J.W., Zoller, W.H., Duce, R.A. and Benson, C.S. (1967). Lead and halogens in pollution aersols and snow from Fairbanks, Alaska. Atmos. Environ., 1, 105.

World Health Organisation (1971). International Standards for Drinking Water, 3rd edition, WHO, Geneva.

## APPENDIX 1. WEIR CALIBRATION

Prior to installation of weirs on site, all four weir tanks were calibrated to obtain an accurate head-to-flow relationship, which could then be utilised for calibration of flow recorders. The following procedure was adopted. Once each tank had been fully fitted with an inlet pipe, baffles etc. as described in section 2.3.2, each in turn was set up in the laboratory so that an adequate supply of water to match expected on-site flows could be directed into the weir inlet. The tank was arranged so that flow leaving the weir for a timed period could be retained and weighed. The tank was then carefully levelled across and along the length of the tank. The zero pointer (Fig. 2.8) was then set level with the invert of the V-notch by means of a simple instrument especially constructed from the author's design for the purpose. The zero pointer fixing nut was then firmly tightened.

Water was then admitted to the tank and its level adjusted until the tip of the zero pointer just touched the surface. A depth gauge, measuring from 0-160 mm in increments of 0.05 mm, was positioned next to the dip tube support (Fig. 2.10) and its tip adjusted so that it just touched the surface at zero head. A range of measured flows was then passed through the tank, and head measurements taken each time, once flow had stabilised. The maximum head measureable with one depth gauge was 160 mm. Using two, this could be increased to 188 mm, equivalent to a flow of about 5.3 $ls^{-1}$. Although less than the full range possible with the notches fitted, this was considered an acceptable upper limit. The calibration curve obtained for the untreated runoff wier is shown in Fig. A1.

Since $\log_{10}$ head is linearly related to $\log_{10}$ flow in a V-notch weir, the best fitting straight line to the data was obtained by least squares linear regression on the logarithmic form of the data. For the UTR weir, the equation obtained was

$$\log_{10}F = -2.3751 + 2.4224 \log_{10}H \qquad (r = 0.999976)$$

where $F$ = flow ($ls^{-1}$)

$H$ = head (cms)

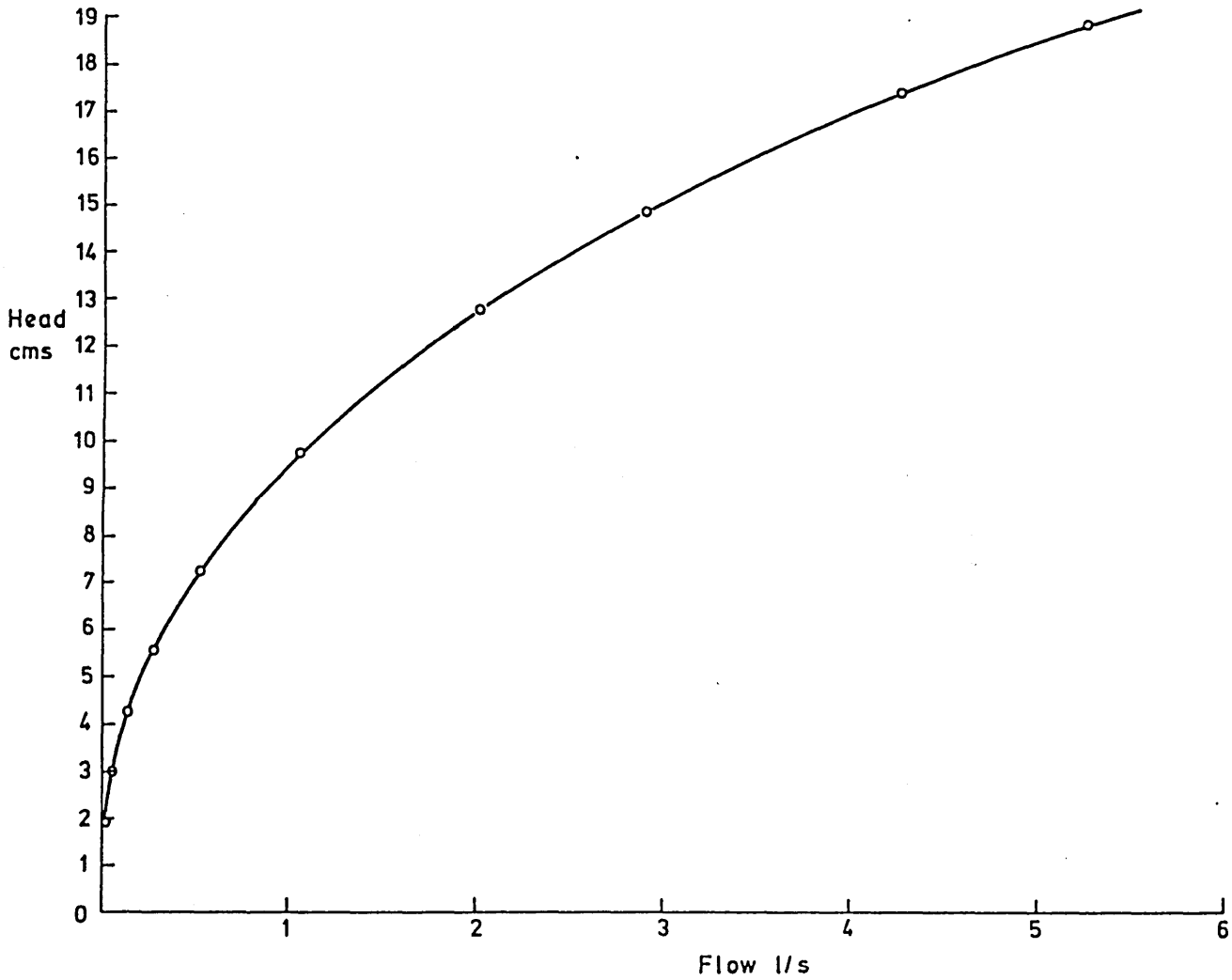



Figure A.1 Rating curve for untreated runoff weir

This is the logarithmic equivalent of

$$F = 4.216 \times 10^{3} \times H^{2.4224} ls^{-1}$$

which is closely analagous to the British Standards Institution (BSI; 1965) discharge equation for a thin plate V-notch weir with notch angle 28°4':

$$Q = C\ 8/15\ \tan(\theta/2)\sqrt{2g}\ H^{2.5}$$

where $Q$ = discharge ($m^3 s^{-1}$)
$C$ = coefficient of discharge (dimensionless)
$\theta$ = notch angle
$g$ = gravitational constant ($ms^{-2}$)

When BSI size criteria for weirs are met, values of C are derived from tables in the standard. Since each weir was calibrated individually, however, any slight deviations from the tabulated values of C due to non-compliance of the weir tanks with the size criteria were automatically accounted for in the experimentally-derived calibration equation.

Occasionally during the sampling period flows exceeded the calibrated range of the weir, although only for short peak periods. In these circumstances, a hypothetical peak shape was fitted by eye to the hydrograph above the calibrated limit, taking into account the time between the rising and falling limbs, the shape of the hydrograph in the calibrated range beneath the peak, and the shape of other typical peaks from events within the calibrated range.

Reference: British Standards Institution (1965). British Standard Specification 3680, Methods of Measurement of liquid flow in open channels, Part 4A: Thin plate weirs and venturi flumes.

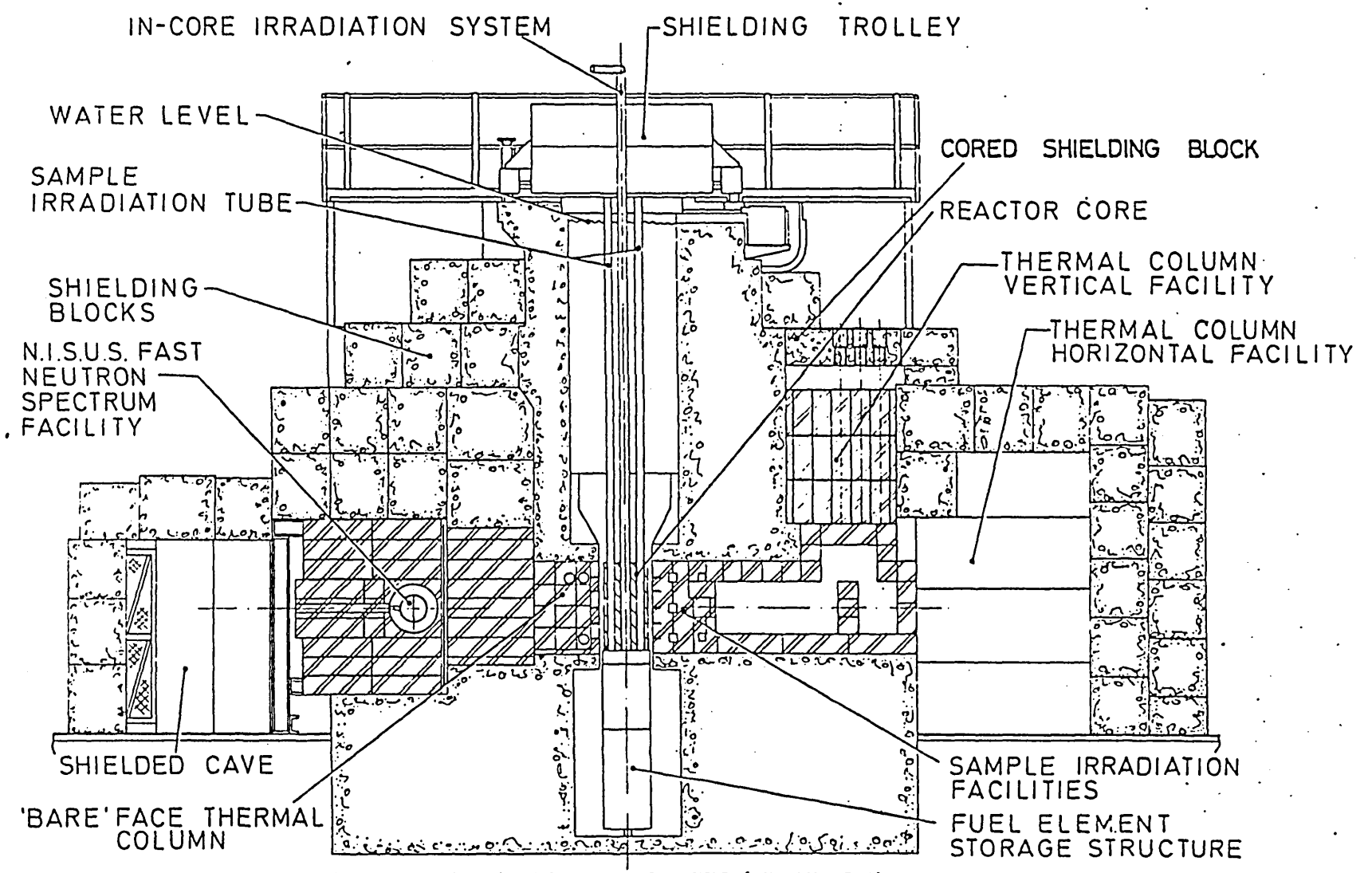



Figure A2(i) REACTOR EXPERIMENTAL FACILITIES (ELEVATION)

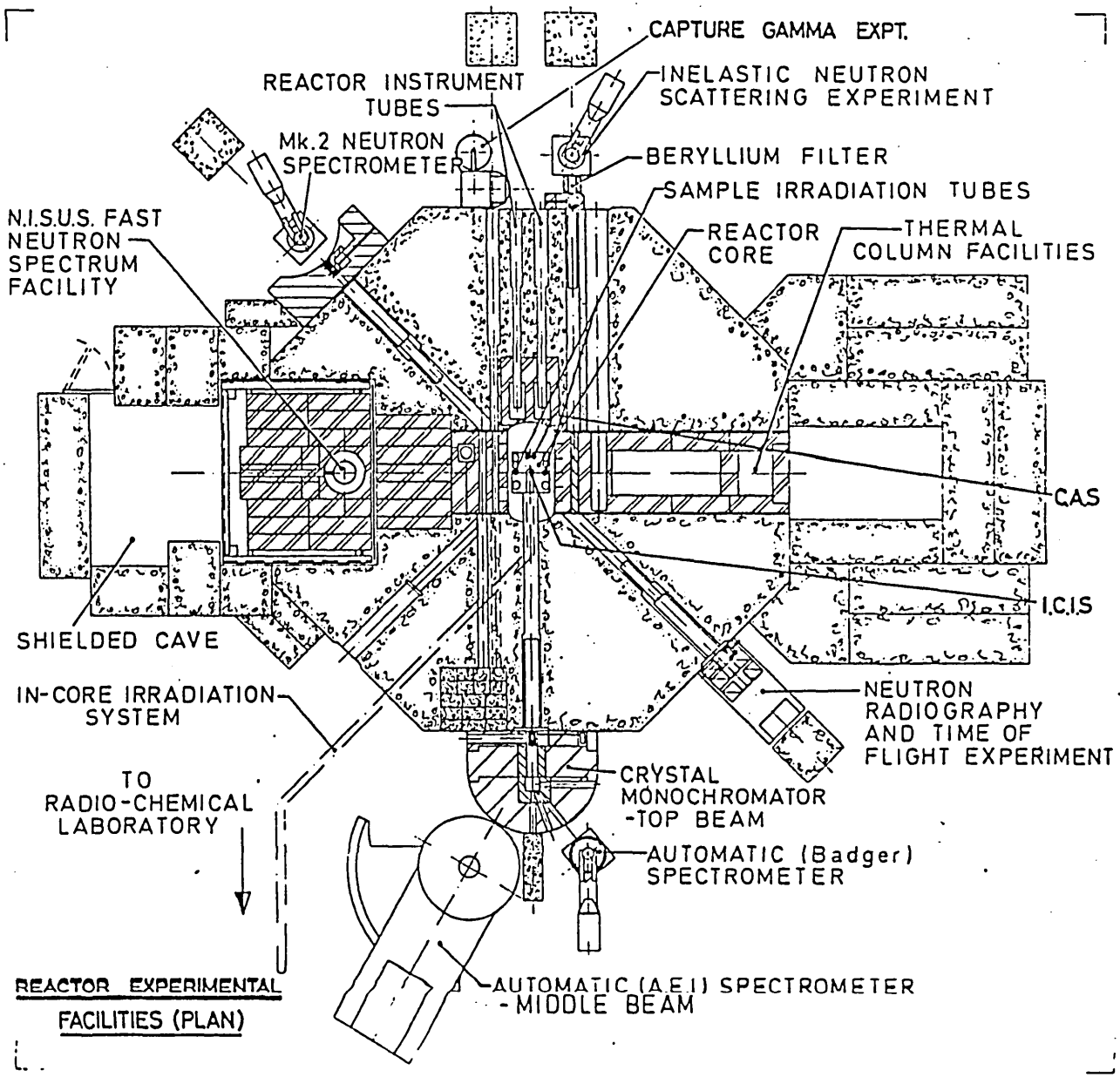



Figure A2(ii) REACTOR EXPERIMENTAL FACILITIES (PLAN)

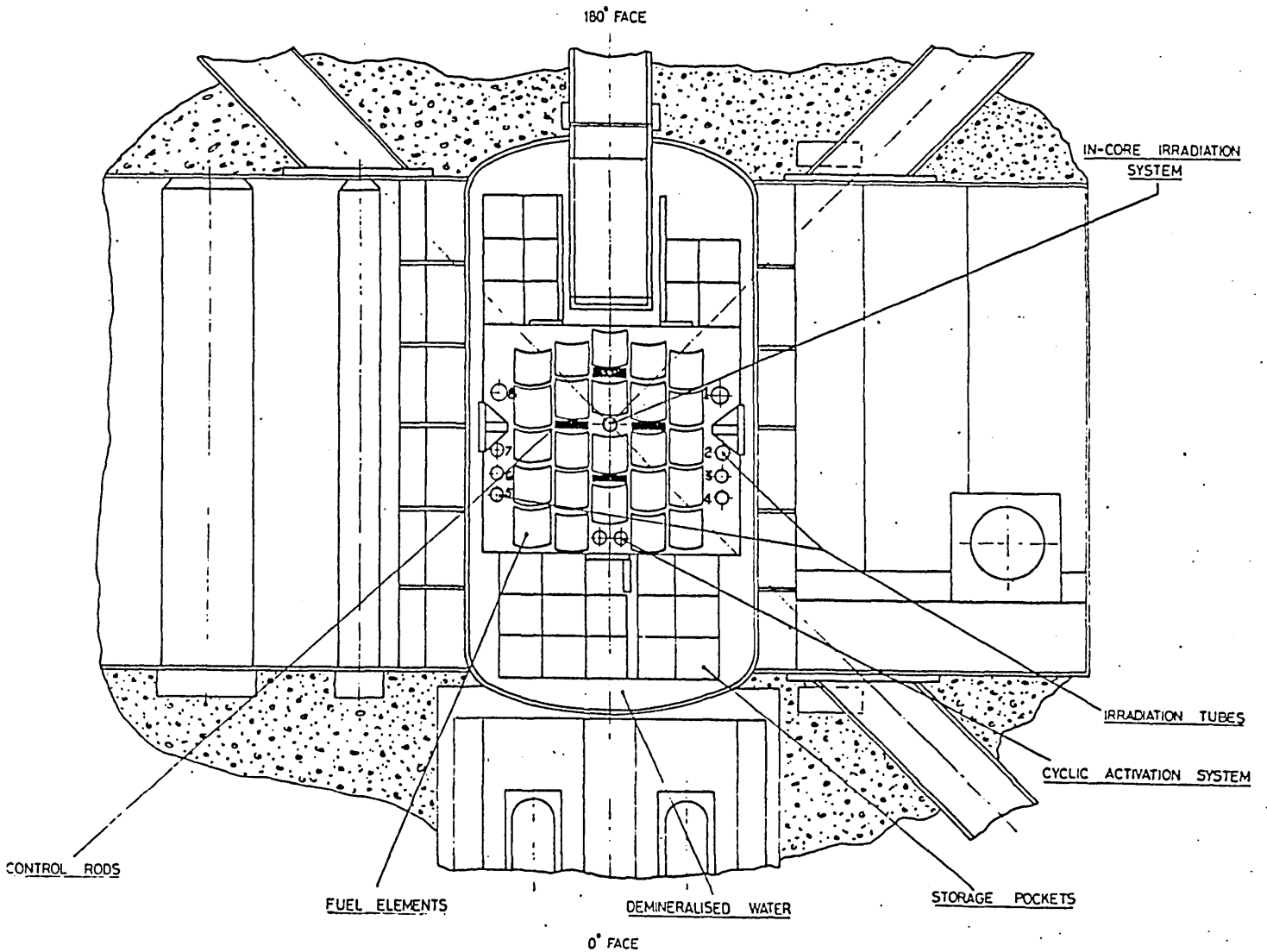



Figure A2(iii) REACTOR CORE (PLAN)

APPENDIX 3. HYDROLOGICAL AND ENVIRONMENTAL DATA FOR SAMPLED EVENTS

| Event Number | Date | Duration of flow (h) | TEV (l) | % TEV Sampled | RVS (mm) | RVS (l) | PFDS ($l s^{-1}$) | MFDS ($l s^{-1}$) | 1/RT ($h^{-1}$) | VFDS (vehicles $min^{-1}$) | ADPT (vehicles x $10^3$) | ADP (h) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| W1 | 7/11/80 | 4.40 | 3370 | 96 | 4.06 | 3220 | 0.46 | 0.24 | 0.78 | 3.6 | 296.60 | 220.07 |
| W2 | 14/11/80 | 5.64 | 3520 | 89 | 4.03 | 3200 | 0.62 | 0.20 | 0.24 | 38.2 | 18.78 | 8.46 |
| W3 | 15/11/80 | 3.68 | 5470 | 96 | 6.62 | 5260 | 1.04 | 0.42 | 0.72 | 26.7 | 14.48 | 16.71 |
| W4 | 9/ 1/81 | 3.68 | 3150 | 92 | 3.67 | 2910 | 0.54 | 0.26 | 3.13 | 35.5 | 89.21 | 69.90 |
| W5 | 17/ 1/81 | 1.87 | 628 | 56 | 0.44 | 350 | 0.24 | 0.15 | 2.86 | 21.3 | 21.18 | 24.48 |
| W6 | 18/ 1/81 | 4.15 | 1700 | 68 | 1.45 | 1150 | 0.21 | 0.12 | 2.13 | 29.4 | 15.59 | 22.32 |
| W7 | 21/ 1/81 | 10.33 | 6340 | 92 | 7.35 | 5830 | 0.58 | 0.19 | 0.23 | 27.4 | 82.27 | 64.11 |
| W8 | 8/ 2/81 | 3.82 | 1190 | 91 | 1.37 | 1090 | 0.24 | 0.07 | 0.29 | 26.5 | 7.16 | 4.47 |
| W9 | 9/ 2/81 | 1.33 | 474 | 90 | 0.54 | 427 | 0.13 | 0.09 | 1.69 | 25.1 | 16.02 | 13.71 |
| W10 | 9/ 2/81 | 4.34 | 2400 | 71 | 2.15 | 1710 | 0.41 | 0.20 | 0.57 | 25.1 | 13.38 | 7.93 |
| W11 | 22/ 2/81 | 2.71 | 1310 | 97 | 1.61 | 1280 | 0.34 | 0.14 | 4.00 | 18.3 | 384.74 | 302.47 |
| W12 | 27/ 2/81 | 0.85 | 221 | 86 | 0.24 | 189 | 0.10 | 0.07 | 6.67 | 25.7 | 195.54 | 128.57 |
| W13 | 28/ 2/81 | 5.55 | 2940 | 39 | 1.45 | 1150 | 0.22 | 0.15 | 0.31 | 3.5 | 3.40 | 8.23 |
| S1 | 23/ 5/81 | 0.84 | 220 | 75 | 0.21 | 164 | 0.09 | 0.09 | 4.00 | 6.9 | 53.37 | 32.84 |
| S2 | 23/ 5/81 | 3.20 | 1270 | 83 | 1.33 | 1060 | 0.27 | 0.14 | 1.00 | 28.5 | 6.85 | 6.70 |
| S3 | 24/ 5/81 | 0.86 | 1050 | 89 | 1.17 | 931 | 1.41 | 0.62 | 7.14 | 24.6 | 33.65 | 28.00 |
| S4 | 24/ 5/81 | 1.35 | 1090 | 92 | 1.26 | 1000 | 1.16 | 0.22 | 10.00 | 28.8 | 4.41 | 2.72 |
| S5 | 25/ 5/81 | 3.38 | 4670 | 53 | 3.12 | 2470 | 1.27 | 0.33 | 0.53 | 4.9 | 7.23 | 12.25 |
| S6 | 9/ 7/81 | 1.21 | 1910 | 95 | 2.29 | 1820 | 1.19 | 0.69 | 7.69 | 30.6 | 519.80 | 375.65 |
| S7 | 11/ 7/81 | 0.71 | 473 | 97 | 0.58 | 460 | 0.39 | 0.22 | 5.00 | 27.4 | 50.88 | 40.01 |
| S8 | 17/ 7/81 | 0.75 | 1880 | 99 | 2.34 | 1860 | 4.91 | 0.79 | 10.00 | 44.7 | 206.01 | 149.56 |
| S9 | 22/ 7/81 | 3.14 | 1540 | 93 | 1.80 | 1431 | 0.25 | 0.14 | 2.22 | 36.0 | 146.90 | 110.99 |
| S10 | 6/ 8/81 | 1.83 | 2280 | 93 | 2.80 | 2220 | 0.90 | 0.42 | 6.67 | 33.7 | 172.48 | 124.05 |
| S11 | 6/ 8/81 | 3.48* | 14700 | 41 | 7.58 | 6020 | ~7.0 | 3.46 | 6.67 | 27.4 | 1.45 | 0.88 |
| S12 | 12/ 9/81 | 2.63* | 6740 | 98 | 8.35 | 6630 | ~6.4 | 0.91 | 1.54 | 5.0 | 37.79 | 25.36 |

TEV = total event volume; RVS = runoff volume sampled; PFDS = peak flow during sampling; MFDS = mean flow during sampling; 1/RT = 1/rise Time; VFDS = vehicle flow during sampling; ADPT = antecedent dry period traffic total; ADP = antecedent dry period. Terms defined fully in Table 5.10. * ±0.42 h.

## APPENDIX 4. DEPOSITION SAMPLING DETAILS

| Sampling Period | Date (1981) | Exposure Time (h) | Total Traffic Count ($\times 10^3$) | Mean Vehicle Flow (vehicles $hr^{-1}$) | Total Rainfall (mm) |
|---|---|---|---|---|---|
| 1 | 10/6-26/6 | 376.9 | 510.2 | 1353 | 10.7 |
| 2 | 7/7-10/7 | 73.5 | 101.4 | 1379 | 3.8 |
| 3 | 24/7- 3/8 | 236.2 | 325.9 | 1380 | 26.3 |
| 4 | 3/8- 8/8 | 125.5 | 173.1 | 1379 | 29.0 |
| 5 | 12/8-17/8 | 120.0 | 171.7 | 1431 | 0.0 |

APPENDIX 5. RUNOFF LOADING DATA

| Event Number | TS (g) | TVS (g) | $Cl^-$ (g) | TSS (g) | Pb (mg) | Zn (mg) | Cd (mg) | COD (g) | $Br^-$ (g) | **$\Delta Br^-$ (g) |
|---|---|---|---|---|---|---|---|---|---|---|
| W1 | 308 | - | 51 | - | - | - | - | 367 | 1.26 | 1.26 |
| W2 | 942 | - | 174 | 323 | 1300 | 1010 | - | 334 | - | - |
| W3 | 1480 | - | 131 | 490 | 2290 | 1330 | - | 281 | 1.46 | 1.45 |
| W4 | 6620 | - | 2850 | 811 | 4240 | 3920 | 35.2 | - | 4.19 | 3.01 |
| W5 | 1840 | 100 | 975 | 42 | 201 | 470 | 10.3 | - | 0.62 | 0.21 |
| W6 | 3920 | 218 | 2090 | 155 | 770 | 1020 | 17.0 | - | 1.70 | 0.83 |
| W7 | 2980 | 595 | 832 | 940 | 3700 | 3120 | 8.1 | - | 1.51 | 1.20 |
| W8 | 2700 | 252 | - | 280 | - | - | - | - | - | - |
| W9 | 3340 | 213 | - | 122 | - | - | - | - | - | - |
| W10 | 704 | 152 | - | 287 | - | - | - | - | - | - |
| W11 | 13500 | 726 | 7130 | 190 | 695 | 4420 | 97.1 | 317 | 5.54 | 2.56 |
| W12 | 618 | 50 | 260 | 25 | 93 | 316 | 4.2 | 42 | 0.30 | 0.19 |
| W13 | 2130 | 133 | 974 | 194 | 725 | 793 | 18.9 | 178 | 1.34 | 0.94 |
| S1 | - | - | 6 | 8 | - | - | - | - | 0.16 | NA |
| S2 | 227 | <180 | 16 | 110 | - | - | - | 133 | 0.56 | " |
| S3 | - | - | 17 | 599 | - | - | 8.5 | - | 0.67 | " |
| S4 | - | - | 17 | 306 | - | - | 0.5 | - | 0.63 | " |
| S5 | - | - | 25 | 464 | 1540* | - | - | - | 0.90 | " |
| S6 | 627 | 210 | 35 | 386 | 1470 | 2530 | 19.3 | 351 | 1.92 | " |
| S7 | 188 | 60 | 15 | 21 | 92 | 431 | 3.2 | 123 | 0.85 | " |
| S8 | - | - | 25 | 4300 | 8080 | 3920 | 35.6 | 631 | 1.41 | " |
| S9 | 445 | 67 | 30 | 107 | 578 | 1260 | - | 457 | 1.80 | " |
| S10 | - | - | 23 | 1060 | 1010 | 2530 | - | 414 | 1.40 | " |
| S11 | - | - | 10 | 4350 | 8010 | 4480 | - | 367 | 0.39 | " |
| S12 | - | - | 29 | 2080 | 5840 | 2840 | - | 1020 | 1.65 | " |

Note: Data have been rounded up where appropriate

** winter $Br^-$ loads adjusted for salting

NA = not applicable

* dissolved fraction estimated

APPENDIX 6. RUNOFF FLOW-WEIGHTED MEAN (FWM) CONCENTRATIONS

| Event Number | TS ($mgl^{-1}$) | TVS ($mgl^{-1}$) | $Cl^-$ ($mgl^{-1}$) | TSS ($mgl^{-1}$) | Pb ($\mu gl^{-1}$) | Zn ($\mu gl^{-1}$) | Cd ($\mu gl^{-1}$) | COD ($mgl^{-1}$) | $Br^-$ ($mgl^{-1}$) | **$ABr^-$ ($mgl^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| W1 | 96 | - | 16 | - | - | - | - | 114 | 0.39 | 0.39 |
| W2 | 294 | - | 54 | 101 | 406 | 317 | - | 104 | - | - |
| W3 | 282 | - | 25 | 93 | 436 | 253 | - | 54 | 0.28 | 0.28 |
| W4 | 2270 | - | 978 | 279 | 1460 | 1350 | 12.1 | - | 1.44 | 1.04 |
| W5 | 5250 | 285 | 2790 | 119 | 574 | 1340 | 29.5 | - | 1.77 | 0.61 |
| W6 | 3412 | 189 | 1820 | 135 | 670 | 887 | 14.8 | - | 1.48 | 0.72 |
| W7 | 510 | 102 | 143 | 161 | 635 | 535 | 1.4 | - | 0.26 | 0.21 |
| W8 | 2480 | 232 | - | 258 | - | - | - | - | - | - |
| W9 | 7810 | 499 | - | 287 | - | - | - | - | - | - |
| W10 | 413 | 89 | - | 168 | - | - | - | - | - | - |
| W11 | 10600 | 569 | 5590 | 149 | 544 | 3470 | 76.0 | 248 | 4.34 | 2.00 |
| W12 | 3270 | 266 | 1380 | 134 | 490 | 1670 | 22.0 | 222 | 1.57 | 1.00 |
| W13 | 1850 | 116 | 849 | 169 | 632 | 691 | 16.5 | 155 | 1.17 | 0.82 |
| S1 | - | - | 36 | 51 | - | - | - | - | 0.95 | NA |
| S2 | 215 | <40 | 15 | 104 | - | - | - | 126 | 0.53 | " |
| S3 | - | - | 19 | 644 | - | - | - | - | 0.72 | " |
| S4 | - | - | 18 | 305 | - | - | - | - | 0.63 | " |
| S5 | - | - | 10 | 188 | 624* | - | - | - | 0.36 | " |
| S6 | 345 | 116 | 19 | 212 | 808 | 1390 | 10.6 | 193 | 1.06 | " |
| S7 | 410 | 130 | 33 | 46 | 200 | 938 | 7.0 | 268 | 1.85 | " |
| S8 | - | - | 13 | 2310 | 4350 | 2110 | 19.1 | 340 | 0.76 | " |
| S9 | 311 | 47 | 21 | 74 | 404 | 883 | - | 319 | 1.26 | " |
| S10 | - | - | 10 | 478 | 1010 | 1140 | - | 186 | 0.63 | " |
| S11 | - | - | 1 | 723 | 1330 | 745 | - | 61 | 0.06 | " |
| S12 | - | - | 4 | 313 | 880 | 429 | - | 154 | 0.25 | " |

Note: Data have been rounded up where appropriate

** winter $Br^-$ loads adjusted for salting

NA = not applicable

* dissolved fraction estimated

APPENDIX 7. SIEVE SOLIDS DATA

| Mesh Size | SAMPLING RUN NUMBER AND DATE (1981) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SS1 (19/2-3/3) | | SS2 (3/3-16/3) | | SS3(3/4-15/4) | | SS4(1/5-11/5) | | SS5(22/5-2/6) | | SS6(2/6-10/6) | |
| (μm) | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing |
| 1600 | 214.70 | 57.0 | 238.65 | 78.2 | 43.32 | 78.0 | 71.58 | 81.4 | 18.41 | 96.2 | 6.50 | 93.2 |
| 400 | 206.14 | 15.7* | 572.43 | 25.9 | 45.63 | 54.9 | 229.31* | 21.9 | 108.08* | 73.8 | 33.75 | 58.1 |
| 318 | 24.65 | 10.8 | 87.50* | 17.9 | 14.29 | 47.7 | 9.74 | 19.4 | 105.13* | 52.1 | 6.10 | 51.8 |
| 253 | 13.52 | 8.1 | 73.46* | 11.2 | 18.10 | 38.5 | 7.24 | 17.5 | 82.46* | 35.0 | 8.35 | 43.1 |
| 154 | 25.22 | 3.0* | 71.20* | 4.7 | 53.68 | 11.3 | 33.65* | 8.7 | 97.09* | 14.9 | 30.31 | 11.6 |
| 100 | 15.02 | 0.0* | 51.26* | 0.0 | 22.28 | 0.0 | 33.70* | 0.0 | 72.22* | 0.0 | 11.11 | 0.0 |
| Mesh Size | SS7 (10/6-15/6) | | SS8 (26/6-10/7) | | SS9(3/8-12/8) | | SS10(12/8-27/8) | | SS11(11/9-16/9) | | SS12(25/9-1/10) | |
| (μm) | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing | Weight on Sieve (g) | % Passing |
| 1600 | 3.37 | - | 19.16 | 57.1 | 145.97 | 61.9 | 66.63 | 75.1 | 134.19 | - | 82.35 | 71.4 |
| 400 | 0.30 | - | 11.59 | 31.1 | 16.27 | 57.6 | 104.04 | 36.3 | 95.46* | - | 44.53 | 55.9 |
| 318 | 0.57 | - | 1.93 | 26.8 | 66.91 | 40.2 | 15.56 | 30.5 | NM | - | 38.98 | 42.4 |
| 253 | 0.77 | - | 2.43 | 21.4 | 46.45 | 28.0 | 25.86 | 20.8 | " | - | 29.06 | 32.3 |
| 154 | 12.58* | - | 6.36 | 7.1 | 68.10* | 10.2 | 36.93 | 7.0 | " | - | 61.11* | 11.1 |
| 100 | NM | - | 3.18 | 0.0 | 39.22* | 0.0 | 18.80 | 0.0 | " | - | 31.98* | 0.0 |

* Sieve blocked NM = No mesh

## APPENDIX 8. EVALUATION OF FLASK SHAKER METHOD FOR OIL EXTRACTION

Four sieve solid subsamples were used to determine the optimum number of extractions necessary with the flask shaker method. The subsamples were taken from run number SS2, mesh sizes 318, 253, 154 and 100 μm. The results are presented in Fig. A8, and indicate that nearly all the oil was removed after three extractions. Thus four extractions were considered sufficient for general use. The number of extractions necessary did not appear to be affected by the level of oil content.

To compare the flask shaker method with the Soxhlet method, both methods were used to determine the oil content of two sets of five sieve solids samples taken from sampling runs SS2 and SS4 respectively. The results are shown in Table A8. The overall mean percentage difference of the flask shaker results compared with Soxhlet results was -8.7%. In view of the advantages of the flask shaker method (i.e. savings in time and no heating requirements), this difference was considered to be within acceptable limits.

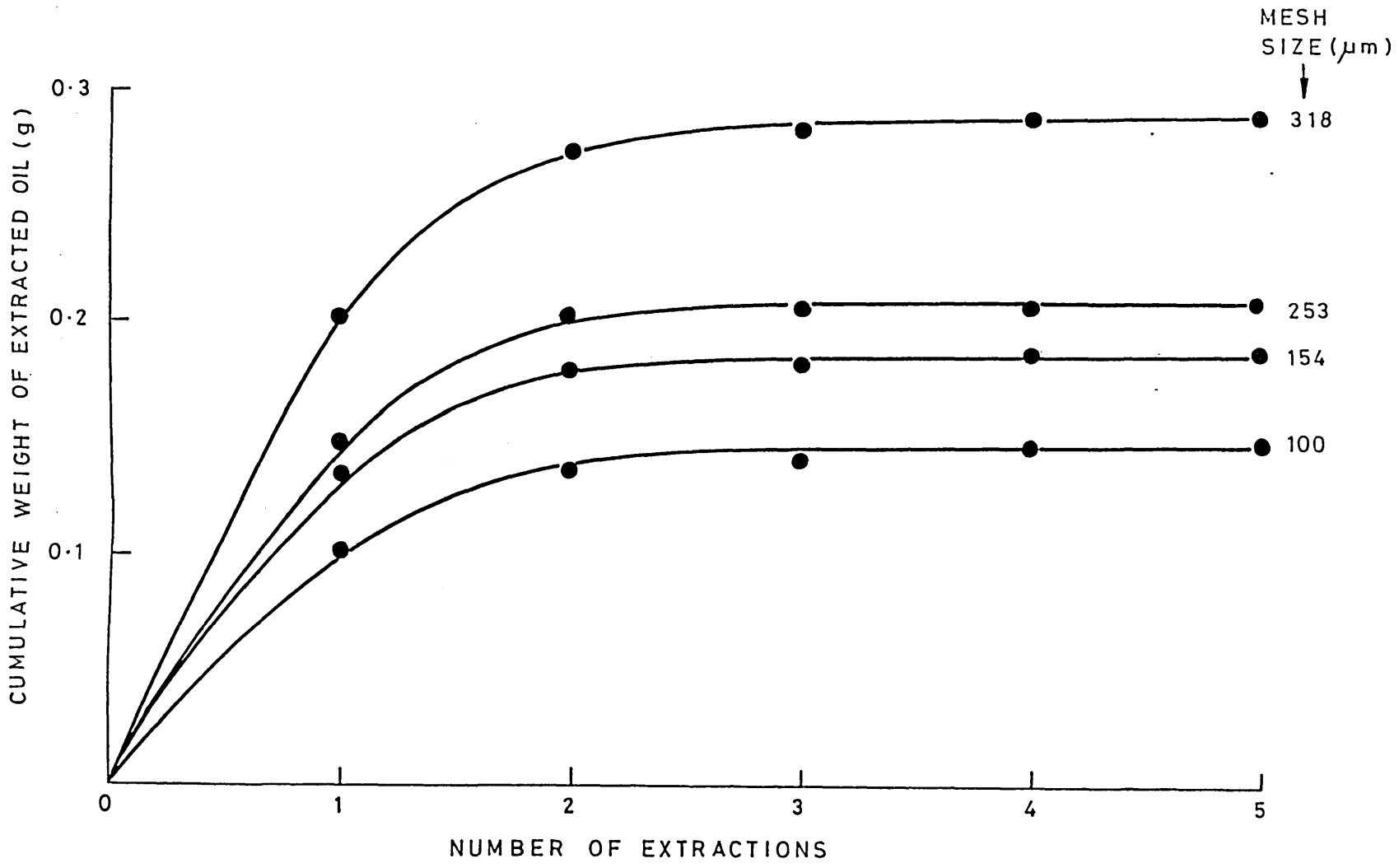



Figure A.8 Results of flask shaker efficiency tests

TABLE A8 : Comparison between flask shaker and Soxhlet methods

| Mesh Size (μm) | SAMPLE SS2 | | | SAMPLE SS4 | | |
|---|---|---|---|---|---|---|
| | Oil Content (mg $g^{-1}$) | | % Difference w.r.t. Soxhlet | Oil Content (mg $g^{-1}$) | | % Difference w.r.t. Soxhlet |
| | Flask Shaker | Soxhlet | | Flask Shaker | Soxhlet | |
| 400 | 55.0 | 70.4 | -21.9 | 30.8 | 44.4 | -30.6 |
| 318 | 90.1 | 100.8 | -10.6 | 148.1 | 168.5 | -12.1 |
| 253 | 95.8 | 81.2 | +18.0 | 120.9 | 108.4 | +11.5 |
| 154 | 75.8 | 81.8 | -7.3 | 81.0 | 84.0 | -3.6 |
| 100 | 61.2 | 75.6 | -19.0 | 94.4 | 106.2 | -11.2 |
| | | | $\bar{x}$ = -8.2 | | | $\bar{x}$ = -9.2 |
| | | | Overall mean difference = -8.7% | | | |

w.r.t. = with respect to

APPENDIX 9. AIR FILTER DATA

| Sampling Run Number | Date (1981) | Volume of Air ($m^3$) | Br Concentration ($\mu g\ m^{-3}$) | Pb Concentration ($\mu g\ m^{-3}$) | Cl Concentration ($\mu g\ m^{-3}$) | Br/Pb | Cl/Br |
|---|---|---|---|---|---|---|---|
| 1 | 3/2-10/3 | 14.77 | 0.63 | 1.80 | 3.10 | 0.35 | 4.92 |
| 2 | 3/3-16/3 | 44.31 | 0.14 | 0.23 | 0.91 | 0.61 | 6.50 |
| 3 | 16/3-30/3 | 23.51 | 0.49 | 0.94 | 2.80 | 0.52 | 5.71 |
| 4 | 30/3- 3/4 | 11.77 | 0.38 | 0.68 | 0.56 | 0.56 | 1.47 |
| 5 | 15/4- 1/5 | 61.00 | 0.28 | 0.53 | 1.63 | 0.53 | 5.82 |
| 6 | 1/5-11/5 | 40.64 | 0.55 | 1.32 | 1.59 | 0.42 | 2.89 |
| 7 | 11/5-22/5 | 44.62 | 0.54 | 1.21 | 1.23 | 0.45 | 2.28 |
| 8 | 26/6-10/7 | 23.59 | 0.96 | 2.09 | 2.61 | 0.46 | 2.72 |
| 9 | 10/7-17/7 | 36.07 | 1.06 | 2.04 | 1.45 | 0.52 | 1.37 |
| 10 | 17/7-28/7 | 78.08 | 1.17 | 2.07 | 1.27 | 0.57 | 1.09 |
| 11 | 3/8-12/8 | 41.63 | 0.82 | 1.71 | 1.29 | 0.48 | 1.57 |
| 12 | 12/8-19/8 | 9.30 | 0.89 | 1.77 | 0.23 | 0.50 | 1.38 |
| 13 | 19/8-27/8 | 35.56 | 0.43 | 0.89 | 0.92 | 0.48 | 2.14 |
| 14 | 27/8- 2/9 | 21.52 | 0.12 | 0.28 | 0.84 | 0.43 | 7.00 |
| 15 | 2/9-11/9 | 30.84 | 0.34 | 0.71 | 1.20 | 0.48 | 3.53 |

APPENDIX 10. DETAILS OF CATCHMENTS REFERRED TO IN FIGURES 8.1A AND 8.1B (after Mance, 1982)

| Catchment Name and Abbreviation | Total Area (ha) | Impervious Area (ha) | Population Per Impervious (ha) | Annual Rainfall (mm) | Type of Area |
|---|---|---|---|---|---|
| Clifton Grove, Nottingham (CG) | 10.6 | 5.5 | - | - | Recent semi-detached housing |
| Welbeck, Nottingham (W) | 16 | 5.6 | - | - | Recent terraced housing (built 1960) |
| Rise Park, Nottingham (RP) | 62 | 19 | - | - | Recent mixed housing with some construction continuing |
| Shephall, Stevenage (S) | 155 | 33 | 291 | 472 | Recent mixed housing (built 1950-1960) |
| Chelmsley Wood, Birmingham (CW) | 107 | 37 | 311 | 787 | Recent mixed housing |
| Oxhey, Nr Watford (O) | 247 | 49 | 257 | 578 | Recent semi-detached housing |
| Graham's Park, Hendon (GP) | 350 | 137.2 | 87 | 660 | Mixed housing with light industry and urban motorway |
| Stevenage New Town (ST) | 2350 | 704* | 100* | 472 | Mature to recent mixed housing and industry with some construction continuing |

* estimated

Note: For M1 data in Fig. 8.1A, concentrations presented are arithmetic means of FWM values from Appendix 6, except for $Cl^-$, where an overall annual FWM value has been used. For loading data in Fig. 8.1B, load per mm of runoff values were derived from Appendix 5 for each event and parameter, annual arithmetic means taken (for each parameter except $Cl^-$ - see Fig. 8.1B) and multiplied by an estimated annual runoff of 518 mm.

*ANNEX II*

**Characteristics of surface water intended for the abstraction of drinking water**

| | Parameters | | A1 G | A1 I | A2 G | A2 I | A3 G | A3 I |
|---|---|---|---|---|---|---|---|---|
| 1 | pH | | 6·5 to 8·5 | | 5·5 to 9 | | 5·5 to 9 | |
| 2 | Coloration (after simple filtration) | mg/l Pt scale | 10 | 20 (O) | 50 | 100 (O) | 50 | 200 (O) |
| 3 | Total suspended solids | mg/l SS | 25 | | | | | |
| 4 | Temperature | ° C | 22 | 25 (O) | 22 | 25 (O) | 22 | 25 (O) |
| 5 | Conductivity | µs/cm$^{-1}$ at 20 °C | 1 000 | | 1 000 | | 1 000 | |
| 6 | Odour | (dilution factor at 25 °C) | 3 | | 10 | | 20 | |
| 7* | Nitrates | mg/l $NO_3$ | 25 | 50 (O) | | 50 (O) | | 50 (O) |
| 8 (1) | Fluorides | mg/l F | 0·7 to 1 | 1·5 | 0·7 to 1·7 | | 0·7 to 1·7 | |
| 9 | Total extractable organic chlorine | mg/l Cl | | | | | | |
| 10* | Dissolved iron | mg/l Fe | 0·1 | 0·3 | 1 | 2 | 1 | |
| 11* | Manganese | mg/l Mn | 0·05 | | 0·1 | | 1 | |
| 12 | Copper | mg/l Cu | 0·02 | 0·05 (O) | 0·05 | | 1 | |
| 13 | Zinc | mg/l Zn | 0·5 | 3 | 1 | 5 | 1 | 5 |
| 14 | Boron | mg/l B | 1 | | 1 | | 1 | |
| 15 | Beryllium | mg/l Be | | | | | | |
| 16 | Cobalt | mg/l Co | | | | | | |
| 17 | Nickel | mg/l Ni | | | | | | |
| 18 | Vanadium | mg/l V | | | | | | |
| 19 | Arsenic | mg/l As | 0·01 | 0·05 | | 0·05 | 0·05 | 0·1 |
| 20 | Cadmium | mg/l Cd | 0·001 | 0·005 | 0·001 | 0·005 | 0·001 | 0·005 |
| 21 | Total chromium | mg/l Cr | | 0·05 | | 0·05 | | 0·05 |
| 22 | Lead | mg/l Pb | | 0·05 | | 0·05 | | 0·05 |
| 23 | Selenium | mg/l Se | | 0·01 | | 0·01 | | 0·01 |
| 24 | Mercury | mg/l Hg | 0·0005 | 0·001 | 0·0005 | 0·001 | 0·0005 | 0·001 |
| 25 | Barium | mg/l Ba | | 0·1 | | 1 | | 1 |
| 26 | Cyanide | mg/l Cn | | 0·05 | | 0·05 | | 0·05 |

| | Parameters | | A1 G | A1 I | A2 G | A2 I | A3 G | A3 I |
|---|---|---|---|---|---|---|---|---|
| 27 | Sulphates | mg/l $SO_4$ | 150 | 250 | 150 | 250 (O) | 150 | 250 (O) |
| 28 | Chlorides | mg/l Cl | 200 | | 200 | | 200 | |
| 29 | Surfactants (reacting with methyl blue) | mg/l (laurylsulphate) | 0·2 | | 0·2 | | 0·5 | |
| 30* (2) | Phosphates | mg/l $P_2O_5$ | 0·4 | | 0·7 | | 0·7 | |
| 31 | Phenols (phenol index) paranitraniline 4 aminoantipyrine | mg/l $C_6H_5OH$ | | 0·001 | 0·001 | 0·005 | 0·01 | 0·1 |
| 32 | Dissolved or emulsified hydrocarbons (after extraction by petroleum ether) | mg/l | | 0·05 | | 0·2 | 0·5 | 1 |
| 33 | Polycyclic aromatic hydrocarbons | mg/l | | 0·0002 | | 0·0002 | | 0·001 |
| 34 | Total pesticides (parathion, BHC, dieldrin) | mg/l | | 0·001 | | 0·0025 | | 0·005 |
| 35* | Chemical oxygen demand (COD) | mg/l $O_2$ | | | | | 30 | |
| 36* | Dissolved oxygen saturation rate | % $O_2$ | > 70 | | > 50 | | > 30 | |
| 37* | Biochemical oxygen demand ($BOD_5$) (at 20 °C without nitrification) | mg/l $O_2$ | < 3 | | < 5 | | < 7 | |
| 38 | Nitrogen by Kjeldahl method (except $NO_3$) | mg/l N | 1 | | 2 | | 3 | |
| 39 | Ammonia | mg/l $NH_4$ | 0·05 | | 1 | 1·5 | 2 | 4 (O) |
| 40 | Substances extractable with chloroform | mg/l SEC | 0·1 | | 0·2 | | 0·5 | |
| 41 | Total organic carbon | mg/l C | | | | | | |
| 42 | Residual organic carbon after flocculation and membrane filtration (5 μ) TOC | mg/l C | | | | | | |
| 43 | Total coliforms 37 °C | /100 ml | 50 | | 5 000 | | 50 000 | |
| 44 | Faecal coliforms | /100 ml | 20 | | 2 000 | | 20 000 | |
| 45 | Faecal *streptococci* | /100 ml | 20 | | 1 000 | | 10 000 | |
| 46 | Salmonella | | Not present in 5 000 ml | | Not present in 1 000 ml | | | |

I = mandatory.
G = guide.
O = exceptional climatic or geographical conditions.
* = see Article 8 (d).

(1) The values given are upper limits set in relation to the mean annual temperature (high and low).
(2) This parameter has been included to satisfy the ecological requirements of certain types of environment.

*ANNEX I*

Definition of the standard methods of treatment for transforming surface water of categories A1, A2 and A3 into drinking water

*Category A1*

Simple physical treatment and disinfection, e.g. rapid filtration and disinfection.

*Category A2*

Normal physical treatment, chemical treatment and disinfection, e.g. pre-chlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination).

*Category A3*

Intensive physical and chemical treatment, extended treatment and disinfection e.g. chlorination to break-point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone, final chlorination).

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Reference: Council of the European Communities (1975). Council Directive of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the member states, Directive 75/440/EEC. Off. J. Eur. Comm., L194, 26.

# APPENDIX 12. BROMIDE IN URBAN RUNOFF - WATER QUALITY CONSIDERATIONS

C.J. SOLLARS, C.J. PETERS and R. PERRY

In Effects of Waste Disposal on Groundwaters and Surface Water (Proceedings of the Exeter IAHS Symposium, July 1982). IAHS Publication No. 139.

*Effects of Waste Disposal on Groundwater and Surface Water* (Proceedings of the Exeter Symposium, July 1982). IAHS Publ. no. 139.

# Bromide in urban runoff — water quality considerations

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ABSTRACT The significance of bromide present in urban runoff and its impact on water quality with respect to trihalomethanes in water supplies is discussed. A well-defined road catchment has been used to examine the occurrence and sources of bromide in runoff, precipitation and air. Significantly higher levels of bromide than usually occur in surface and groundwaters have been found. Detailed studies have identified vehicle emissions as a major source of bromide, while seasonal variations have been related to deicing salt applications. The bromide present in runoff is almost entirely in the dissolved state. The implications of this work regarding movement of bromide within the hydrological cycle and the effects on surface waters receiving large quantities of urban runoff are considered.

## INTRODUCTION

In recent years, trihalomethanes (e.g. $CHCl_3$, $CHClBr_2$) have been detected in most potable water supplies (Symons et al., 1975). This has caused concern over the possible long term health effects which this may pose, in view of the suspected carcinogenicity and mutagenicity of these and related compounds. The formation of halogenated organic compounds takes place during the chlorination stage of water treatment. The chlorine added reacts readily with bromide and naturally-occurring humic material present in raw waters to produce trihalomethanes and other halogenated compounds. Vinogradov (1959), Bowen (1966) and Luong et al. (1980) have reported bromide levels in surface waters ranging between 0.02 and 0.2 mg $l^{-1}$.

There are several potential sources of bromide in surface waters. These include urban runoff containing bromide (arising from dibromoethane in petrol as a scavenger for lead)and the occurrence of bromide as an impurity in the rock salt used for road de-icing. Other possible courses apart from a geochemical and marine background contribution are runoff from agricultural land and industrial or domestic point source effluents.

It has become clear in recent years that runoff from urban areas is often highly contaminated and a considerable source of organic and inorganic pollutants in surface waters (e.g. Hajas et al., 1978). In the particular case of lead contamination, it is now well established that in the absence of specific industrial sources the

major contributor of this element to urban runoff is automobile exhaust. Furthermore, it is claimed that this is also a source of atmospheric bromine, particularly in urban areas, and studies by Winchester et al. (1967), Moyers et al. (1972) and O'Connor et al. (1977) have demonstrated a close relationship between airborne levels of bromine and lead.

The work presented in this paper has investigated the significance of two possible sources of bromide in urban runoff, dibromoethane in petrol and bromide in de-icing salt. A length of motorway in a rural area was selected in order to isolate as far as possible vehicle-related effects on urban runoff quality. This study examined (a) the effect of bromine in vehicle emissions and bromide in deicing salt on bromide levels in motorway surface runoff and (b) the potential contribution of urban runoff generally to bromide levels in surface waters draining urban areas. In order to distinguish between motorway and non-motorway sources of Pb and Br in runoff the following types of sample were analyzed for Pb, Br and Cl: (a) filtered air, (b) total deposition, (c) road surface dust, (d) tyre rubber and (e) bitumen. In addition to the Br-Pb relationship, attention was given to the relationship between Br and Cl since the ratio of the two elements in natural systems is fairly well documented, so that large divergences from the ratio expected can be indicative of the presence of non-natural Br.

## SAMPLING SITE AND EXPERIMENTAL PROCEDURES

### Sampling Site and Sampling Techniques

The site used for this work is situated about 56 km northwest of London beside the M1 motorway which links London and Birmingham, and has been used for previous water quality studies (Pope et al., 1978, 1979). The M1 carries one of the heaviest flows of traffic in Britain, usually between 25000 and 40000 vehicles per 24 h day, with a high proportion of heavy goods vehicles. The road runs in a generally southeast to northwesterly direction at the study site. The drainage area under study (figure 1) consists of a short (54 m) straight length of 3 lane southbound carriageway and hard shoulder of total width 14.8 m, with cross and longitudinal carriageway slopes of 2.5% and 0.61% respectively. The road is surfaced in hot rolled asphalt, and the edge of the tarred area is delineated by a 60° sloping kerb face, 100 mm deep. The area from which runoff is collected is assumed to be a parallelogram of approximately 793 $m^2$, measuring 53.6 m × 15.2 m, with angles between the two sides of 70° and 103° respectively. Appropriate flow monitoring and runoff sampling facilities are installed just below the lowest point of the drained area.

Total deposition samples (rain + dry deposition combined) were also collected at the site and at a control site 600 m west from the motorway, using polypropylene collecting funnels and bottles of cross-sectional area 669 $cm^2$ in grid formation (see figure 1). Air was sampled at 6.7 m from the edge of the hard shoulder by being drawn through 0.22 μm membrane filter at a steady rate (approximately 3 l $min^{-1}$). Sampling periods ranged between 5 and 16 days.

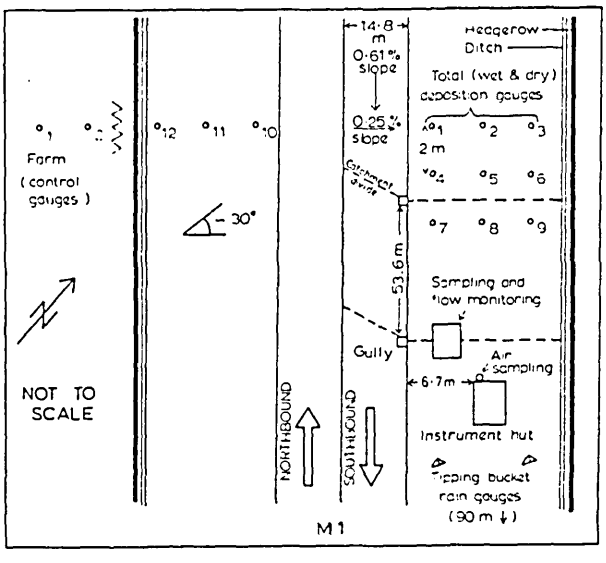



FIG. 1 The motorway sampling site.

Road dust samples and bitumen samples were also collected within the drainage area. Runoff and air samples were collected during both winter and summer, while deposition and dust samples were collected in summer only.

## Analytical Procedures

All types of sample, e.g. runoff, rain etc. were analyzed for lead, bromine and chlorine. Lead analysis was carried out using flameless atomic absorption spectrophotometry, employing the necessary sample pretreatment techniques (Krishnamurty et al., 1976). Instrumental neutron activation analysis employing automatic gamma ray spectrometry was used for bromine and chlorine determinations, except in samples containing >200 $mgl^{-1}$ sodium.

In these cases, owing to excessive sodium activity after irradiation, only Br could be determined by gamma ray counting, so that a standard volumetric method had to be used for Cl determinations (Department of the Environment, 1972). Water samples were concentrated by freeze drying and pelleting prior to irradiation. Experimental errors for lead, bromide and chloride values are generally within the range of ±10%, 12% and 10% respectively, except for road dust samples where bromide and chloride levels are close to detection limits, giving a maximum error of ±60%.

Suspended solids were determined by filtration through 0.45 μm cellulose membrane filters. This pore size has been chosen since this is now widely accepted as a standard classification for "filterable" and "unfilterable" parameters in water quality studies (Hunt, 1979) and hence has been adopted for this work. Contamination by or loss of Pb and Br during the filtration procedure is minimal.

## RESULTS AND DISCUSSION

### Sources of Bromide in Runoff

Air samples, total deposition, road surface dust and bitumen from the site were analyzed for Pb, Br and Cl in order to ascertain the chief sources of these elements in the drainage area. Samples of tyre rubber were also analyzed for these elements. Total deposition background samples were collected 600 m west from the site. The data obtained are given in Table 1.

### Air Samples

Considering data for air samples first (column 1), it is clear that both mean Pb and Br levels are an order of magnitude higher than concentrations found in air at other rural sites in the UK, whereas Cl values are close to background levels (Cawse, 1981).

Almost all the petrol sold in the UK contains the additives tetraethyl- amd tetramethyl lead, and dibromo- and dichloroethane. These are added in proportion to give a mole ratio of Pb:Br:Cl in petrol of 1:1:2. With this mix, the major forms of Pb and Br to be found in fresh exhaust particulate matter are usually PbBrCl and $2PbBrCl\text{-}NH_4Cl$ (Hirschler *et al.*, 1957; Habibi, 1973) both having a Br/Pb ratio of 0.39. These workers employed techniques which specifically excluded the collection of non-particulate matter. The mean Br/Pb value of 0.54 found in air sampled continuously 6.7 m from the edge of the carriageway in this work is comparable with this value. The figure of 0.39 refers of course only to particulate combustion products. The slightly higher value found in this work may reflect the presence of some form of vehicle-generated non-particulate bromine (such as HBr) which could be adsorbed by the sampling filter. This effect was found by Li and Smith (1976), who found, using a similar filtering apparatus to this work, Br/Pb ratios in fresh exhaust between 0.48 and 0.60.

Overall, therefore, it is reasonable to conclude that the high Pb and Br levels found in air samples at this site arise directly from exhaust emissions from traffic on the M1. The low Cl/Br ratio compared with background values is additional evidence for this, indicating a major road-related increase in airborne Br compared with Cl, which has a wider variety of sources in the environment than Br and is thus less affected by vehicle-related sources alone.

### Total Deposition Samples

Column 2, Table 1 gives Pb, Br and Cl data for total deposition samples (rain and dry deposition combined). These values were obtained by combining data from soluble and insoluble fractions after filtration and analysis. Br and Pb levels are clearly much greater than background, while Cl values are also higher but not to the same extent as Br. Comparison of the Cl/Br value at three roadside gauges compared with background also shows a very significant decrease, and undoubtedly the similarity of trends in the deposition data with those found in air data confirm that a substantial input of Pb and Br to the gauges is vehicle-generated.

TABLE 1 Br, Pb and Cl in samples taken at the motorway site

| Column | 1 | 2 | | | | 3 | 4 | |
|---|---|---|---|---|---|---|---|---|
| Sample Type | Air | Total (Rain + Dry Deposition) | | | | Road Surface Dust | Tyre Rubber | Bitumen |
| Units | Samples $\mu g\ m^{-3}$ | $mg\ m^{-2}\ day$ Distance from carriageway (m) | | | | $mg\ g^{-1}$ | $mg\ g^{-1}$ | $mg\ g^{-1}$ |
| | | 0.5 | 2.5 | 4.5 | 600 m | | | |
| No. of samples | 15 | | 27 | | | 8 | 4 | 3 |
| Total Pb (mean) | 1.1 | 3.95 | 1.77 | 1.50 | 0.03 | 3.11 | 0.054 | 0.004 |
| (Range) | (0.22-2.1) | (1.64-6.53) | (1.37-1.85) | (0.76-1.82) | (0.02-0.04) | (2.03-6.84) | (0.045-0.062) | (0.001-0.006) |
| Background | 0.04-0.16[a] | | * | | | 0.006-0.1(soil)[b] | - | - |
| Total Br (mean) | 0.59 | 0.63 | 0.37 | 0.21 | 0.02 | - | <0.005 | <0.01 |
| (Range) | (0.12-1.17) | (0.33-1.05) | (0.26-0.51) | (0.17-0.23) | (0.016-0.024) | (<0.03-0.18) | - | - |
| Background | 0.03-0.08[a] | | * | | | 0.005(soil)[c] | - | - |
| Total Cl (mean) | 1.52 | 7.91 | 6.04 | 3.72 | 1.68 | - | 0.72 | <0.13 |
| (Range) | (0.92-3.1) | (4.48-14.26) | (3.45-11.75) | (1.77-9.40) | (1.05-2.19) | (<0.13-0.89) | (0.62-0.89) | - |
| Background | 1.7-3.9[a] | | * | | | ~0.1(soil)[c] | - | - |
| Br/Pb (w/w) | 0.54 | 0.19 | 0.24 | 0.21 | 0.80 | - | <0.12 | <4.01 |
| (Range) | (0.42-0.71) | (0.14-0.32) | (0.16-0.31) | (0.13-0.26) | (0.55-1.2) | (0.004-0.08) | - | - |
| Background | 0.44[a] | | * | | | - | - | - |
| Cl/Br (w/w) | 3.4 | 15.9 | 18.7 | 18.4 | 81.3 | - | >138 | - |
| (Range) | (1.1-7.0) | (10.3-27.1) | (10.9-31.0) | (9.98-40.9) | (55.3-98.2) | (<0.87->30) | - | - |
| Background | 46.7- 75[a] | | * | | | ~20(soil)[c] | - | - |

(a) Cawse (1981)
(b) Motto et al. (1970) and references therein
(c) Bowen 1966
* See values for 600 m

Of particular interest, however, is the noticeable decrease in the Br/Pb ratio from a mean of 0.54 in air to a value in the region of 0.2 in total deposition. This indicates that, if all Br and Pb found in the gauges arises directly from ambient air, then some loss of Br with respect to Pb has taken place, or, if airborne Pb and Br alone are not responsible for the total Br and Pb load, then another source of Pb is contributing to the total Pb load. It was clear from the appearance of the sample solids found in the gauges that a significant part of the total deposition often consists of road surface dust and soil distributed over the gauges by vehicle-generated turbulence. The Br/Pb values found for road dust in this work (<0.004-0.08) indicate that deposition of this dust in the gauges would significantly lower the overall Br/Pb ratio.

The very low Br/Pb ratios found in road dust indicate that leaching of Br from deposited particulates takes place. Examination of the soluble/insoluble division between Pb and Br in total deposition samples showed that although the overall Br/Pb ratio lies between 0.21 and 0.24, 80% or more of Pb was solid associated in most samples, while 90% or more of Br was in soluble form. Br/Pb ratios on deposition solids gave a mean value of 0.03, compared with 0.54 for air samples. Thus both road dust and total deposition samples strongly indicate loss of Br with respect to Pb, and that this loss may take the form of Br solubilisation from essentially insoluble particulate matter which retains the vast majority of its Pb content. The behaviour of these two elements in surface runoff will thus be dependent on different factors, with Pb movement being related to sediment transport and Br dependent on the rate of solubilization and subsequent dilution, with important consequences from a water quality standpoint. This topic is discussed more fully in the next section.

The remaining types of sample analyzed for possible contribution of Br, Pb and Cl to runoff (tyre rubber and bitumen, columns 4 and 5) clearly show that none of them can be regarded as significant contributors of either Br or Pb, although tyre rubber could influence the prevailing Cl concentrations to some extent. Its negligible Br content, however, eliminates it as a significant source of Br and especially as a factor causing low Cl/Br levels in other samples.

In conclusion, therefore, it is clear that since vehicle emissions are the only major source of Pb at the sampling site, and in view of the close correlation of Br levels with Pb in air and deposition samples, vehicle exhaust must also be a major contributor of Br to runoff from the study area.

## Behaviour of Br, Pb and Cl in Runoff

Table 2 presents a summary of data gathered from 11 storm events, 7 from a winter period (January-March) and 4 during summer (May-July). The data covers 110 single samples, although some were composited on a flow weighted basis prior to analysis. Mean concentration values of parameters given were derived from total mass loadings for (a) all winter and (b) all summer storms sampled respectively, divided by the total volume for the two respective periods. Br/Pb ratios were calculated from original mass loadings.

TABLE 2 Range of Br, Pb and related parameters in motorway runoff

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| | Mean Flow Rates $ls^{-1}$ | Mean Duration of Storms Sampled HRS | Mean Total Br Concn. $mgl^{-1}$ | Mean Total Cl Concn. $mgl^{-1}$ | Conductivity Range µS | Mean Total Pb Concn. $mgl^{-1}$ | Mean TSS Concn. $mgl^{-1}$ | Mean Solid Assoc. Pb Concn. $\mu g g^{-1}$ | Br/Pb |
| Winter Events (7) (84 Samples) | 0.12 | 3.15 | 2.13 | 2486 | 910-22000 | 0.64 | 154.6 | 3892 | 3.33 |
| Range of Individual Values | 0.07-0.48 | 0.49-5.42 | 0.55-6.0 | 366-6714 | | 0.22-2.75 | 77.1-717.0 | 1157-4097 | 0.46-19.17 |
| Summer Events (4) (26 Samples) (19 for Pb) | 0.37 | 1.88 | 0.58 | 13.2 | 38-552 | 0.59 | 219 | 2484 | 0.98 |
| Range of Individual Values | 0.07-0.67 | 1.2-3.42 | 0.04-1.55 | 1.4-38.4 | | 0.07-0.79 | 40.7-341 | 1324-4679 | 0.07-16.55 |

The different distribution of Br, Cl and Pb between soluble and insoluble phases in all runoff samples was often more marked than in total deposition. Eighty per cent or more of Pb but 1.5% or less of total Br and Cl in samples was found to be solid associated. Thus in comparing data for Br, Cl and Pb between winter and summer events, it must be noted that dilution is a much more important factor in changing Br and Cl concentrations, while flow-related phenomena such as surface scour will be of correspondingly greater importance for suspended solids concentrations and therefore the majority of Pb movement.

## Seasonal Variations

Comparison of the mean values of the parameters given for winter and summer periods clearly show the expected enormous influence of deicing salt application on conductivity and chloride values.

The suspended solids show some seasonal variation, the mean winter value being about 30% less than that for summer. The mean total Pb levels for both winter and summer are, however, similar, whereas the mean winter Br level is about four times higher than for summer. This winter level is also about ten times higher than the highest background levels found in surface waters.

Although the mean weekly traffic flows during the two sampling periods were very similar, a combination of other environmental and hydrological factors appear to be among the major causes of the large seasonal difference between mean Br concentrations. Deicing salt as applied contains in the region of 230 mg kg-1 bromide. Taking into account a small amount of "non-salt background" chloride, calculated from summer chloride levels and assuming the remainder to arise from deicing salt, the winter chloride load accounted for 49% of the total winter bromide load, leaving a "residual" bromide mean concentration of 1.09 mg $l^{-1}$. This is still, however, about twice the summer value of 0.58 mg $l^{-1}$. In summer, however, the hydrological regime at this site is markedly different from winter, with short, heavy storms making a greater contribution to rainfall than in winter, when periods of prolonged, moderate rain are more common. Thus winter mean flow rates (Table 2, column 1) are lower and duration of storms longer (column 2) than in summer, and these differences must be taken into account in comparing winter and summer Br levels even when the effect of deicing salt has been discounted.

A highly simplified attempt to account for these differences can be taken by considering mean loadings per event (for winter and summer periods) rather than concentrations alone. Taking mean loading rate as the product of mean concentration and mean flow for winter and summer periods respectively, these values for Br are 0.131 and 0.215 mg $s^{-1}$ (excluding Br arising from deicing salt for winter values). The mean load per event must, of course, take into account the mean duration of events. Thus, multiplying winter and summer loading rates by the respective mean duration of events sampled (column 2), we have figures of 1480 (winter) and 1452 (summer) mg Br removed per event. This would indicate that there is no significant seasonal difference in the amount of "non-salt" Br

available for removal from the road, which, since the majority of this Br arises from vehicle emissions, is in accordance with the similarity of traffic flows found for the two periods.

Pb and Suspended Solids

In view of the very high proportion of sample Pb associated with suspended solids, it is convenient to consider these two values together. The scouring effect of higher mean flows during summer sampling is reflected in the increase of the summer mean TSS value compared with that of winter which, unlike the bromide concentrations, show no effects of dilution, despite a summer mean flow three times that of winter. The mean summer Pb concentration, however, is about the same as that in winter, but this is accounted for largely by a substantial decrease in the concentration of Pb on the suspended solids themselves. Visual examination of the solids revealed that for events with high peak flows a significiant proportion of the solids consists of larger, gritty particles (>0.5 mm diam) which clearly arise from road surface degradation, soil etc. rather than combustion processes and would therefore tend to be low in Pb. Thus the Pb concentration in solids is often effectively diluted with respect to events with lower mean flows. Clearly , the overall Br/Pb ratio for winter and summer, 3.33 and 0.98 respectively, reflects to a large extent the factors affecting the concentrations of the two elements outlined above.

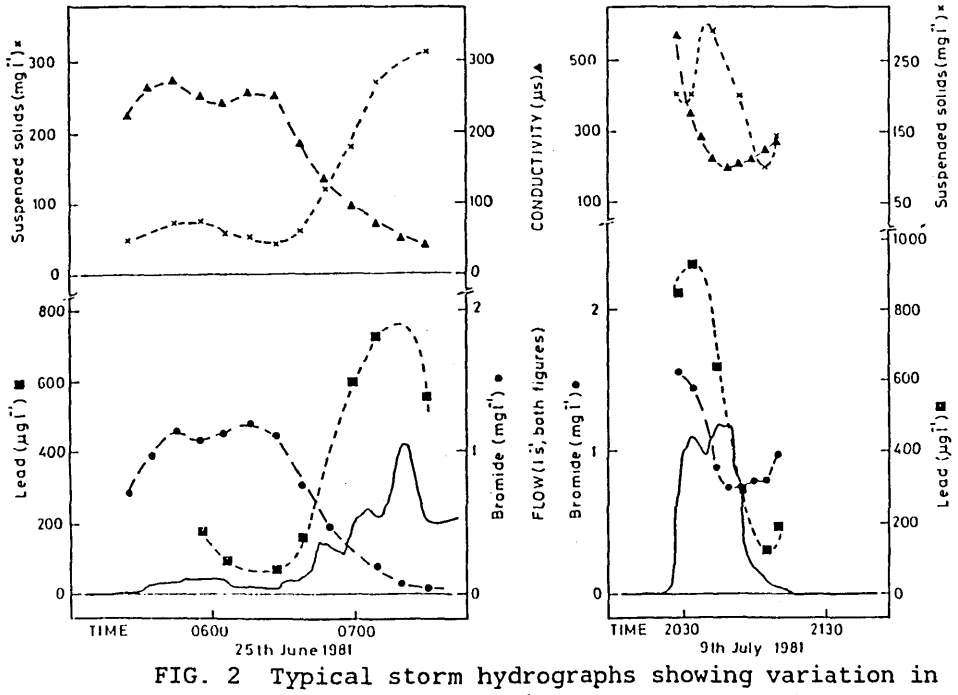



FIG. 2 Typical storm hydrographs showing variation in contaminant levels with time.

Figure 2 presents Br, Pb, suspended solids and conductivity data

in detail for two summer storm events which illustrate some of the points discussed. The pattern of Pb and suspended solids through both events shows a clear relationship between the two, with suspended solids being markedly increased at high flow values as scouring of the road surface takes effect, while bromide and conductivity levels are more affected by a combination of "first flush" effects and dilution at higher flow rates. The different behaviour of Br and Pb clearly shows a rapid solubilisation of Br from the road surface compared with essentially insoluble Pb, often leading to very high Br/Pb ratios in samples (up to 16.6) compared with air samples. Although some loss of Br from particulate matter in runoff may occur between sample collection and analysis, this could by no means account for the frequently high Br/Pb ratios encountered.

## Water Quality Implications of Bromide in Runoff

In the light of the very different physical and chemical behaviour of Br and Pb in runoff, therefore, it is apparent that their relative impact on any receiving water course will depend on different factors. Bromide, being almost entirely in soluble form, will be transported more easily and therefore more widely than lead.

In urban areas, traffic density will generally be lower than on a major motorway and the rate of initial lead particulate emission and deposition therefore lower, except on the busiest routes. On motorways, however, traffic generated turbulence and generally more exposed conditions will serve to significantly disperse deposited dust and particulate matter away from the road surface, while in more congested urban areas these effects will be greatly reduced. Roadside dust in urban areas has, in addition, been shown to contain lead contents in a range very similar to those found in this work and others (Harrison, 1979 and references therein). Moreover, the general range of lead concentrations found in urban runoff (e.g. Mance & Harman, 1977) is at least as high as those encountered in this work. Very few data exist concerning bromide levels in urban runoff, but in view of the relationship between lead and bromide it is to be expected that runoff from urban areas will contain similar levels to those found in motorway runoff. Thus urban runoff must be seen as a potentially major source of bromide in surface waters, especially during summer after periods of prolonged dry weather when a reasonably intense rain storm over a large urban area may contribute a very significant increase in flow and bromide load to a receiving water under conditions of dry weather flow. This has clear implications for water quality and THM formation during water treatment.

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REFERENCES

Bowen, H.J.M. (1966) Trace Elements in Biochemistry. 177-178, Academic Press, London.

Cawse, P.A. (1981) A Survey of Atmospheric Trace Elements in the UK: Results for 1979, UKAEA, Harwell, AERE-R9886. HMSO, London.

Department of the Environment (1972) In: The Analysis of Raw, Potable and Waste Waters, 73-76. HMSO, London.

Habibi, K. (1973) Characteriziation of particulate matter in vehicle exhaust. Environ. Sci. Technol., 7(3), 223-234.

Hajas, L., Boggs, D.B., Shuckrow, A.J., Quimpo, R.G. (1980) Projecting urban runoff flows and loads. J. Environ. Engng. Div. ASCE, 104 (EE6), 1149-1163.

Harrison, R.M. (1979) Toxic metals in street and household dusts. Sci. Tot. Environ., 11, 89-97.

Hirschler, D.A., Gilbert, F.W., Lamb, F.W., Niebylski, L.M. (1957) Particulate lead compounds in automobile exhaust gas. Indust. and Engng. Chem., 49(7), 1957.

Hunt, D.T.E. (1979) Filtration of Water Samples for Trace Metal Determinations: Technical Report TR104, Water Research Centre, Medmenham, Bucks, UK.

Krishnamurty, K.V., Shpirt, E., Reddy, M.M. (1976) Trace metal extraction of soils and sediments by nitric acid-hydrogen peroxide. At. Abs. Newsletter, 15, 68-70.

Li, T.M., Smith, C.C. (1976) Emissions of sulphuric acid and the nature of halide emitted from a car. Internal Report, Associated Octel Co. Ltd., Ellesmere Port, UK.

Luong, T.L., Peters, C.J., Young, R.J. & Perry, R. (1980) Bromides and trihalomethanes in water supplies. Environ. Technol. Letts., 1, 299-310.

Mance, G., Harman, M.M.I. (1978) The quality of urban storm-water run-off. In: Proc. Int. Conf. on Urban Storm Drainage, Southampton, 1978, 603-617. Pentech Press, London.

Moyers, J.L., Zoller, W.H., Duce, R.A., Hoffman, G.L. (1972) Gaseous bromine and particulate lead, vanadium and bromine in a polluted atmosphere. Environ. Sci. Technol., 6, 68-72.

O'Connor, B.H., Kerrigan, G.C., Thomas, W.W., Pearce, A.T. (1977) Use of bromine levels in airborne particulate samples to infer vehicular lead concentrations in the atmosphere. Atmos. Environ., 11, 635-638.

Pope, W., Graham, N.J.D., Young, R.J., Perry, R. (1978) Urban runoff from a road surface - a water quality study. Prog. Wat. Tech., 10(5/6), 533-543.

Pope, W., Young, R.J., Sollars, C.J., Perry, R. (1979) The distribution of selected heavy metals in a motorway environment. Proc. Int. Conf. on Heavy Metals in the Environment, London, 1979, 230-235. CEP Consultants Ltd., Edinburgh.

Symons, J.M., Bellar, T.A., Carswell, J.K., De Marco, J., Kropp, K.L. Robeck, G.G., Seeger, D.R., Slocum, C.J., Smith, B.L., Stevens, A.A. (1975) National organics reconnaissance survey for halogenated organics. J. Am. Wat. Wrks. Assoc., 67, 634-647.

Vinogradov, A.P. (1959) The Geochemistry of Rare and Dispersed Elements in Soils, 2nd Edn. Consultants Bureau, Inc., New York.

Winchester, J.W., Zoller, W.H., Duce, R.A., Benson, C.S. (1967) Lead and halogens in pollution aerosols and snow from Fairbanks, Alaska. Atmos. Environ., 1, 105-119.