

ERRATA

P. 2	line 27	delete "single", insert "sludge"
P. 5	line 19	delete "additional", insert "addition"
P.12	line 2	delete "conyrol", insert "control"
P.12	line 38	delete "meta-", insert "metal"
P.13	line 36	delete "wastewater", insert "waste water"
P.16	line 5	delete "slusge", insert "sludge"
P.17	line 4	delete "concentrat ons", insert "concentrations"
P.28	line 28	delete "oc", insert "of"
P.29	line 18	delete "Carrondo (1980)" insert "Carrondo <u>et al.</u> , (1980)"
P.32	line 24	delete "UK", insert "U.K."
P.43	line 31	delete "absorption", insert "adsorption"
P.44	line 15	delete "increase", insert "increasing"
P.96	line 9	delete "Water Pollution Control", insert "Treatment"
P.117	line 29	delete "this", insert "This"
P.119	line 10	delete "copper", insert "chromium"
P.138	line 30	delete "4%", insert "3%"
P.138	line 34	delete "4%", insert "14%"
P.187	line 8	delete "liquands", insert "ligands"
P.192	line 16	delete "contining", insert "containing"
P.203	line 22	delete "stoichometrically", insert "stoichiometrically"

INFLUENCE OF DETERGENT BUILDERS ON HEAVY METALS
IN WASTE WATER TREATMENT

A thesis submitted to the University of London
in partial fulfilment of the requirements for
the degree of Doctor of Philosophy in
the Faculty of Engineering

by

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June 1981

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ABSTRACT

The literature on the fate of heavy metals and detergent builders in waste water treatment processes has been reviewed, particularly with respect to the effects of detergent builders on the efficiency of removal of heavy metals.

Experiments have been undertaken with pilot scale primary sedimentation and activated sludge plants located at a full-scale sewage treatment works and fed with raw and settled sewage obtained from the works. The removals of cadmium, chromium, copper, lead, nickel and zinc in primary sedimentation were studied, and were found to be typically 25-50% in conditions designed to simulate normal dry weather flow. However, heavy metal removal efficiencies were found to be adversely affected by introducing higher overflow rates or variable flow conditions. The removals of heavy metals were also influenced by two detergent builders: zeolite type A, an insoluble, inorganic, crystalline aluminosilicate, and nitrilotriacetic acid (NTA), a soluble organic chelating agent. Zeolite type A was removed with efficiencies of approximately 70%, and caused an improvement in the removals of chromium, copper, lead and zinc probably as a result of ion exchange, although cadmium and nickel removals were relatively unaffected. The removal of NTA during primary sedimentation was found to vary between 16 and 40% and its presence in the raw sewage caused a reduction in the efficiencies of several metals but principally those of lead, nickel and zinc.

In the activated sludge pilot plant experiments were undertaken at sludge ages of 4, 9 and 12 d. It was found that when soluble heavy metals were added to the settled sewage optimum removals and the greatest degree of immobilization of heavy metals in the mixed liquor occurred at a single age of 12 d, although when metals were not added optimum removals occurred at the 9 d sludge age. NTA was found to have an adverse effect on heavy metal removal efficiencies unless it was biodegraded. After the introduction of NTA into the system a period of acclimatization occurred prior to the onset of biodegradation, during which time heavy metal removals were reduced. NTA could be almost completely biodegraded by the activated sludge, thus having no effects on heavy metal removal, but transient shock loads were not immediately biodegraded, resulting in the mobilization of heavy metals into the effluent.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr R. Perry for making this study possible. My sincere thanks are also due to Dr J.N. Lester for giving me much of his time for helpful discussion, guidance and encouragement during my studies and throughout the thesis preparation. I am grateful to my colleagues in the Public Health Engineering Laboratory for their encouragement and discussion, in particular to Robert Sterritt for fruitful discussions of metal speciation in the presence of micro-organisms.

I am indebted to the late Mr R. Brannan, the Departmental Superintendent, to Mr. R. Rapley, the workshop foreman and to Mr P.F. Clifford and Mr P. Hart, the electricians, for their outstanding contribution in building and maintaining the pilot plants. The laboratory technician, Mr S. Gupta deserves a special mention for his help in the hard task of keeping the pilot plants running.

To Mrs S. Wright I would like to express my thanks for typing this thesis and for her excellent co-operation throughout this work. My thanks to Miss J. Gurr for preparing the photographs and Mrs H. Guile for the figures.

My appreciation is expressed to the Metropolitan Public Health Division of the Thames Water Authority, in particular to the Manager, Mr E.G. Eves, and the Assistant Manager-Scientific, Mr D.M. Sindall for their co-operation during the pilot plant experimental programme.

I wish to acknowledge with appreciation the financial support from the Pan-American Health Organisation/World Health Organisation for the fellowship received. To CETESB - Companhia de Tecnologia de Saneamento Ambiental and Faculdade de Saúde Pública - USP, São Paulo, Brazil, for whose permission and financial support I am deeply indebted.

However, most of all my thanks are long overdue to my wife, Ivone and my sons Alexandre, Carlos Henrique and Douglas Jose for their love, understanding and patience given throughout my studies.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
ABS	Acrylonitrile-butadiene-styrene
BOD	Biochemical oxygen demand
CIRIA	Construction Industry Research and Information Association
COD	Chemical oxygen demand
conc	Concentration
cm	Centimetre
C	Control
d	Day
DWF	Dry Weather Flow
EDTA	Ethylenediaminetetra-acetic acid
EEC	European Economic Community
Eff	Effluent
Fig	Figure
g	Gram
g	Gravity
h	Hour
Inf	Influent
l	Litre
M	Molar (i.e. 5M = 5 molar solution)
ML	Mixed liquor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
mg	Milligram
min	Minute
ml	Millilitre
mlc	Metre liquid column
mm	Millimetre
mol. wt.	molecular weight
N	Normal (i.e. 0.0625N = 0.0625 normal solution)
nm	Nanometre
NTA	Nitrilotriacetic acid
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
pH	Hydrogen ion concentration
R	Removal

RSD	Relative Standard Deviation or coefficient of variation
s	Second
SS	Suspended solids
STPP	Sodium tripolyphosphate
SVI	Sludge volume index
U.K.	United Kingdom
U.S.A.	United States of America
V/V	Volume for volume
VSS	Volatile suspended solids
%	Percent
µg	Microgram
µl	Microlitre
°C	Degrees Celcius

1. INTRODUCTION

Eutrophication is the enrichment of water by organic and inorganic nutrients resulting in excessive algal and plant growth. It is claimed that phosphorus is the nutrient responsible for much of the excessive growth that is occurring in many natural water bodies, especially lakes (Lee et al., 1978). One consequence of this excessive algal and plant growth is that the hypolimnion becomes depleted of oxygen during the summer months due to decaying organic matter falling from the epilimnion. This oxygen depletion may result in the death of other forms of aquatic life, especially fish, which can have economic consequences for the fishing industry as in the case of Lake Eire in North America (Owens & Wood, 1968). Other consequences of eutrophication and the concomitant increase in the algal population are the reduction in the amenity value of waters overgrown with plant life and the imparting of objectionable tastes and odours to drinking waters often rendering them unpalatable.

The principal nutrients which limit algal growth are carbon, nitrogen, phosphorus, silicon, potassium, trace metals and vitamins (Owens & Wood, 1968). Of these carbon, nitrogen and phosphorus have been studied most, the latter two more extensively than the former (Owens & Wood, 1968). For a substance to be classified as the main cause of algal growth, that substance must be essential for growth and must be present at a limiting concentration (i.e. the concentration of that substance must be stoichiometrically less than the concentration of all the other essential substances). The accepted average stoichiometric ratio of the principal algal nutrients which covers most species commonly encountered is C:N:P = 106:16:1 (Lee et al., 1978), thus relatively small quantities of phosphorus are required in comparison to carbon and nitrogen. It has been reported that most fresh water lakes and impoundments are phosphorus limited (Lee et al., 1978). To control eutrophication it is considered desirable to control the entry of phosphorus into the waters which are at risk (Lee et al., 1978).

Conventional sewage treatment removes approximately 50% of the phosphorus present in the raw sewage (De Renzo, 1978) thus even well treated sewage effluents contain a substantial part of the influent phosphorus concentration. The phosphorus component of sewage or sewage effluent discharges is often considered to be responsible for eutrophication in receiving waters. One important group of phosphorus containing compounds present in domestic waste water are those containing the phosphate group. The phosphate group is divided into two classes, the orthophosphates and the condensed or complex phosphates. Condensed phosphates have a higher proportion of phosphorus pentoxide (P_2O_5) and a lower proportion of sodium oxide (Na_2O) which gives them a lower alkalinity. The main condensed phosphates are:

Tetrasodium pyrophosphate $Na_4P_2O_7$ or $2Na_2O : 1 P_2O_5$

Sodium tripolyphosphate $Na_5P_3O_{10}$ or $2\frac{1}{2}Na_2O : 1\frac{1}{2} P_2O_5$

Sodium tetrakisphosphate $Na_6P_4O_{13}$ or $3 Na_2O : 2 P_2O_5$

Sodium hexametaphosphate $(Na PO_3)_6$ or $3 Na_2O : 3 P_2O_5$

Synthetic detergents utilise in their composition a component referred to as the "builder". The builder most commonly used is one of the condensed phosphates, STPP. As a builder it performs several functions, the main one being the enhancement of the efficiency of the surfactant by the removal of the calcium and magnesium ions. As a chelating agent it sequesters the calcium and magnesium hardness in the water and prevents the deposition of insoluble scums (Environmental Resources Ltd., 1979). All the condensed phosphates and particularly STPP act synergistically with the surfactant to improve the basic cleaning efficiency of the detergent by reducing the critical micelle concentration of the surfactant. They will redissolve insoluble calcium and magnesium salts left embedded in the fibres of the clothes from previous washes, can deflocculate and keep in suspension insoluble materials such as clay by adsorption onto the particles thereby imparting repelling charges and are able to emulsify oily materials (Davidsohn and Milwidsky, 1972). They

have a buffering capacity, provide the correct alkalinity for optimum results and also form complexes with heavy metal ions which might otherwise cause discolouration (Devey and Harkness, 1973). It is therefore clear that the condensed phosphates play a vital role in the detergent formulation. From the detergent manufacturer's stand point they have one drawback which is that they all hydrolyse to orthophosphate, but at differing rates under different conditions. For hexametaphosphates the hydrolysis is quite rapid under washing conditions but for pyrophosphates in the cold it is very slow (a matter of weeks), and for polyphosphates it is somewhere between the two (Davidsohn and Milwidsky, 1972). However, from the environmental stand point the hydrolysis to orthophosphate, which occurs rapidly in sewage, is beneficial in that orthophosphates are more readily removed in tertiary treatment processes than are the polyphosphates (Finstain & Hunter, 1967) and also they do not possess the chelating properties of the polyphosphates.

It was estimated that in 1979 in excess of one million tons of phosphates would have been used in cleaning and conditioning agents in the EEC (Environmental Resources Ltd., 1979). The contribution of detergent phosphorus to the total phosphorus in municipal sewage in the late 1960's and early 1970's was approximately 50% in the U.K., Sweden and the North American continent (Owens and Wood, 1968; Bunch and Ettinger, 1967; Bouveng et al., 1968). In an attempt to control phosphorus discharges in sewage effluents, tertiary treatment involving precipitation has been used to remove phosphorus. Removals of 84 and 91.7% using alum and iron coagulants in tertiary treatment have been reported (De Renzo, 1978). Alternatively pressure has been brought to bear on detergent manufacturers to reduce or remove completely the phosphorus content of their products.

The question as to whether detergent phosphates are the major cause of the increasing eutrophication of natural waters has been debated over a number of years, and as yet there is no clear answer (Jones, 1972). The three main subjects of controversy are:

whether phosphorus is in all (or even the majority of)
cases the limiting nutrient for algal growth,

whether the proportion of phosphorus contributed by detergents to natural waters compared with other sources is significant,

and

whether there would be any noticeable reduction in eutrophication should the phosphate content of detergents be reduced or removed.

Schindler (1977) postulated that phosphorus limitation in any lake was only temporary and that after a sudden increase in its concentration, algae will 'fix' carbon and nitrogen from the atmosphere and correct the nutrient balance. He showed that this was so in experiments on a full scale lake, and that algal growth was ultimately proportional to phosphorus concentration. He pointed out, however, that nitrogen limited lakes would induce more nitrogen fixation than phosphorus limited lakes for the same increase in phosphorus concentration. This would result in greater quantities of the more objectionable nitrogen fixing 'water bloom' blue-green algae, in proportion to the less objectionable phosphorus controlled algae. However, Kuentzel (1969) demonstrated that there was a symbiotic relationship between algae and bacteria. Bacteria require oxygen and yield carbon dioxide; algae require carbon dioxide and yield oxygen. He demonstrated that algal blooms were often preceded by large bacterial blooms and that they were also associated with excessive amounts of decomposable organic matter. The amount of carbon dioxide that could be fixed from the atmosphere or that could come from the dissolved carbonate salts was insufficient for the fast growing algae, but bacteria with enough organic matter were capable of supplying sufficient quantities of carbon dioxide. To support his contention he cited cases where, in the presence of decomposable organic matter and of soluble phosphorus at concentrations of less than $0.01 \text{ mg } \ell^{-1}$ there had been massive algal blooms whereas in other lakes with greater than $0.01 \text{ mg } \ell^{-1}$ of soluble phosphorus but relatively free from organic pollution, there were no algal problems. Hence the availability of carbon dioxide via the action of bacteria on organic matter was essential and thus phosphorus removal would not be effective unless equal emphasis was placed on the removal of organic pollution.

The assessment of which nutrient is limiting in any body of water cannot be done solely on the bases mentioned above, as many other physical, chemical and biological conditions also govern algal growth. For example, bacteria, algae and protozoa are able to store phosphorus far beyond their nutritional requirements by a process known as 'luxury uptake' and release them later usually as a result of changes in pH (Hudson and Marson, 1970). The depth of the water body, exposure to sunlight (Hudson and Marson, 1970), variation in nutrient concentration with depth and variations of nutritional requirements between algal species (Fitzgerald, 1972) are other governing factors. Consequently, although it is quoted in the literature that nuisance due to algal growth in lakes begins to occur when the phosphorus concentration has risen to $0.01 \text{ mg } \ell^{-1}$ (Owens and Wood, 1968; Ferguson, 1968), many inland waters are unaffected by growth at much higher phosphorus concentrations and many begin to be affected at much lower concentrations. A detailed examination of all the characteristics of a water body has to be made, therefore, before phosphorus could be identified as the principal cause of its eutrophication.

The concentration of phosphorus contributed by detergents to natural waters has been widely studied in many countries and compared to the concentrations contributed from other sources. The sources of phosphorus have been identified by Weaver (1969) and are listed in Table 1.

Table 1 - Sources of Phosphorus in Natural Waters (from Weaver, 1969)

Domestic:	Human wastes	}	Discharged through sewage treatment works
	Soaps and detergents		
	Household food wastes		
Industrial			
Other minor sources			
Industrial direct discharges			
Water treatment chemicals			
Urban run-off			
Stormwater			
Agricultural land : Fertilisers and farm waste			
Non-agricultural land : Decaying animals and vegetation			
Groundwater			
Lakes : Sediments			
	Living plants		
Atmosphere : Rain and dust fall			

Reported proportions of the various sources of phosphorus reaching natural waters in different geographical locations are shown in Table 2.

Table 2 - Proportions of Phosphorus from various sources reaching natural waters in various geographical locations

Source of Phosphorus	Percentage from Each Source Reaching Waters			
	U.K. (1)	N.America (2)	U.S.A. (3)	U.S.A. (4)
Waste water excluding detergents, garbage and other human wastes	{ 68 }		{ 22 }	{ 23 }
Detergents in waste water		9		
Garbage and other human wastes		17		
Agricultural land	{ 28 }	59	42	{ 50 }
Non-agricultural land			29	
Urban run-off			6	11.5
Headwaters	4			
Rainfall		{ 15 }	0.4	1
Dry fallout				5
Other atmospheric sources				
Ground water				0.5
Baseflow				9
Other			0.6	

(1) Owens and Wood, 1968

(2) Harrington-Hughes, 1978

(3) Bartsch, 1972

(4) Bond et al., 1974

The portion of the total phosphorus reaching natural waters that emanates from synthetic detergents has been estimated at between 25% and 40% in the U.S.A. (Jones, 1972; Grundy, 1971), approximately 9% for the Great Lakes area of North America (Harrington-Hughes, 1978) and an average of 30% for urban areas rising to 40% for densely populated urban areas in Europe (Environmental Resources Ltd., 1979). Comparing the figures quoted above for the U.S.A. with those in Table 2 it can be seen that there is some disagreement between the various reports over the amount of detergent phosphorus reaching natural waters.

It is not evident whether a reduction in the phosphate content of detergents is going to reduce the concentration of phosphorus in receiving waters sufficiently to affect the nutrient balance and if such an adjustment to the nutrient balance is going to reduce algal

growth in eutrophic waters. Ferguson (1968) calculated that for continental U.S.A., the average of all phosphorus discharged from all sources to the entire U.S.A. streamflow would give an average phosphorus concentration of $0.26 \text{ mg } \ell^{-1}$. If 90% of the detergent phosphate were removed, the concentration would be $0.11 \text{ mg } \ell^{-1}$ and if 100% were removed it would be $0.08 \text{ mg } \ell^{-1}$. He then compared this with the nebulous $0.01 \text{ mg } \ell^{-1}$ limit for eutrophication and concluded that the benefit to be gained from prohibiting detergent phosphates seemed doubtful. Although the calculations are based on very average figures, this does demonstrate that not in all cases is the detergent phosphate the culprit in water enrichment. It should be noted that Sweden has adopted a cautious policy with regard to laying the blame for eutrophication solely on detergent manufacturers, and reduction in phosphate levels in Swedish detergents has developed naturally in an atmosphere of goodwill rather than through legislation (Ferguson, 1968). The U.S. Environment Protection Agency has also concluded from a recent progress report that for the Great Lakes, a ban on detergent phosphates will result in only a small part of the eutrophication problem being solved (Harrington-Hughes, 1978).

It may fairly be concluded that detergent phosphates are in many instances significant in causing eutrophication in natural waters, though in many cases the mechanism of enrichment is a much more complex process than limitation in terms of a single nutrient. Whilst tertiary treatment for phosphate removal is often employed (De Renzo, 1978) there have been strenuous efforts made to find alternative phosphate free detergent builders.

There are two main categories of substitutes, organic and inorganic. Inorganic builders include sodium carbonates, sodium silicates, sodium borate, sodium sulphate, and zeolite (Berth, 1978). Organic builders include aminocarboxylates, such as nitrilotriacetic acid, polymeric polycarboxylates with carbon backbone, ether carboxylates such as carboxymethyloxysuccinate, carboxymethyltartronate and small molecules such as citrates, acetates, and succinates (Matzner *et al.*, 1973a). Four major criteria must be met by a potential substitute, product performance, human safety, environmental safety and economic feasibility (Ashforth and Calvin, 1973; Matzner *et al.*, 1973b). These criteria must be met before they are used on a wide scale. Two potential builders are of particular interest, zeolite type A and NTA.

Zeolite type A, an aluminosilicate is currently being considered as a partial substitute for STPP (Berth, 1978). Although it does not fulfil all the functions of a detergent builder it allows a reduction in the amount of chelating agent needed in detergent formulations. Incorporated into a controlled binary system with STPP it has been reported to enhance washing performance compared with formulations containing only STPP (Berth, 1978; Schwuger and Smolka, 1976). Zeolite type A is a crystalline (cubic) aluminosilicate with a uniform pore size and an internal surface area many times larger than the external surface area (Breck et al., 1956). Due to its molecular sieve properties, zeolite type A has been extensively used in the chemical processing industries (Breck, 1974). It has a typical oxide formula of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$ but, because of the possible occlusion of NaAlO_2 in the structure the silicon to aluminium ratio can vary from 0.7 to 1.2 (Breck, 1974). In contrast to the chelating builders, zeolite type A removes calcium and, to a lesser extent, magnesium ions by ion exchange (Schwuger and Smolka, 1976). Since such a reaction is kinetically controlled the rate of calcium removal by zeolite is several times slower than that of the chelating builders, occurring only after approximately three minutes as opposed to less than one minute for STPP (Henning et al., 1977). For the particles sizes used in detergent formulations the maximum calcium exchange capacity of zeolite is approximately $200 \text{ mg CaO g}^{-1}$ zeolite at 90°C , but only 150 mg g^{-1} at 20°C when no sodium is present in solution (Henning et al., 1977); the corresponding values for MgO are 80 and 15 mg g^{-1} , respectively (Henning et al., 1977). The detergent formulations containing zeolite are manufactured such that, by the end of a washing programme, only 20 to 30% of the calcium exchange capacity of zeolite has been exerted (Henning et al., 1977). It has a specific gravity of 1.99 increasing to 2.05 when completely exchanged for calcium (Breck et al., 1956).

The settleability of zeolite in waste water was studied in static settling tests by Carrondo et al., (1981) and King et al., (1980). The former used 15 cm diameter columns and a zeolite concentration of 30 mg l^{-1} and found that the predicted removal of zeolite in primary sedimentation with 1 and 2 h retention time would be 55 and 69%, respectively. It was also demonstrated that the percentage of sewage solids removed in the static column test was marginally less in the presence of zeolite. Using 10.2 cm diameter columns and zeolite concentration varying from 0 to 100 mg l^{-1} King et al., (1980) concluded that removal of zeolite by primary treatment would be similar to that of other suspended solids. The same author studied sedimentation of zeolite using a 6 l rectangular tank at different

flow rates of raw sewage dosed with $20 \text{ mg } \ell^{-1}$ of zeolite. The flow was adjusted to give detention time of 0.5, 1, 1.5 and 2 h which corresponded to overflow rates of 6.6, 3.3, 2.2 and 1.6 md^{-1} . Using different size particles of zeolite it was found that the removal of zeolite and the smallest 10% size-fraction were 77 and 62%, respectively, for an overflow rate of 1.6 md^{-1} .

Studies of the behaviour of zeolite type A in the activated sludge process concluded that it would not have any detrimental effects and may even increase the settleability of the activated sludge flocs, enhance the removal of ammonia and phosphate and assist the biodegradation of anionic surfactants (Fischer et al., 1978; Hopping, 1978; Carrondo et al., 1980; King et al., 1980). An extensive laboratory research programme was undertaken by King et al., (1980) and Holman and Hopping (1980) to study the effect of zeolite in different types of biological and tertiary treatment. No adverse effect on the performance of laboratory models of activated sludge, trickling filter, septic tank and anaerobic digester were observed. Carrondo (1980), using an activated sludge pilot plant and zeolite type A dosed at 15 and $30 \text{ mg } \ell^{-1}$ found an average removal of 88% and anticipated, in waste water treatment plants comprising primary settling and secondary treatment by activated sludge, removals greater than 80%. In a study employing a package plant serving 81 residences in the U.S.A., Hopping (1978) indicated that total zeolite removals during treatment of 80 to 90% were achieved with inlet concentration varying from 7.6 to $17.1 \text{ mg } \ell^{-1}$. A field study was undertaken by Holman and Hopping (1980) using six package plants (septic tank, plus aerobic stage) each serving an individual home, a further six such systems were used as controls. The test group were supplied with laundry detergent containing approximately 20% sodium zeolite. Removals of 81 to 88% were achieved without any deleterious effects on process efficiency.

The substitute builder that has received most attention in the last 15 years and which has been most widely used is the trisodium salt of NTA. The acid form of NTA is a polycarboxylated amine which is commercially manufactured from ammonia, formaldehyde and hydrogen cyanide (Warren and Malec, 1972). NTA has been the most favoured replacement for STPP because it is a good chelating agent and is therefore efficient in softening the wash water, it will suspend the soil on clothes and it can be produced commercially at a competitive

cost (Jones, 1972). Its disadvantages are that its long term effects are unknown, it cannot be a complete replacement for STPP without the cleaning efficiency of the detergent suffering, and it absorbs moisture which without STPP would result in lumps being formed in the detergent package (Jones, 1972).

The quantity of NTA likely to be encountered in municipal sewerage systems has been widely reported in the literature with quoted figures emanating from actual measurements taken in sewers within areas where NTA is in use and from calculations based on estimated waste water flows and detergent usage. A report to the Great Lakes Research Advisory Board in North America (International Joint Commission, 1978) includes results from a comprehensive review of the literature and shows treatment plant influent concentrations varying from $1.3 \text{ mg } \ell^{-1}$ to $118 \text{ mg } \ell^{-1}$. It was estimated in the report that realistic average concentrations of NTA in sewerage systems would be $5 \text{ mg } \ell^{-1}$ for a 15% NTA content in detergents (with a phosphate level of about 5%) and $10 \text{ mg } \ell^{-1}$ when all the detergent phosphate had been replaced by NTA. A study of considerable interest was conducted by Woodiwiss et al., (1979) who measured the influent NTA concentrations at sewage treatment plants in 13 Canadian cities where NTA-containing detergents are used. The study extended over several years during periods when the percentage of NTA in detergents was 6% and when it was 15%. The concentrations varied considerably from city to city and from month to month, but the geometric mean of the NTA influent levels was $1.7 \text{ mg } \ell^{-1}$ for 6% NTA in detergents and $3.6 \text{ mg } \ell^{-1}$ for 15%. These figures are only slightly below the estimated concentrations in the Great Lakes Report (International Joint Commission, 1978).

The removal of NTA in sewage treatment has also been widely discussed and data reported (International Joint Commission, 1978), removal efficiencies for primary sedimentation and activated sludge are shown in Table 3. Little work has been carried out on removal during primary sedimentation and reports are conflicting. Shumate et al., (1970) in their field study measured an average of 8% loss of NTA in primary sedimentation, but their sampling technique was poor and they concluded that NTA was not significantly removed or biodegraded at the primary stage. Bouveng et al., (1968) on the other hand, with a laboratory scale plant and real sewage found that adding $2 \text{ and } 10 \text{ mg } \ell^{-1}$

Table 3 - Reported efficiencies of NTA removal in municipal waste water treatment facilities (International Joint Commission, 1978).

Waste Treatment Processes	Influent NTA Concentration, (mg ℓ^{-1})	NTA Removal Efficiency %	Notes
Primary Sedimentation	4.8	30	Average for 6-month period from Canadian City
	2.0	58	Average for 6-month period from Canadian City
	1.6	11	Average for 6-month period from Canadian City
Activated Sludge	20	92	Laboratory continuous flow units
	5 and 20	3*	Laboratory studies at 5°C
	5 and 20	66-82	Laboratory studies at 7.5°C
	5 and 20	98	Laboratory studies at 20°C
	--	High	Full scale-effluent < 0.5 mg ℓ^{-1} NTA in winter and summer
	10	90	Laboratory scale
	2.2	61	Full scale, at 14°C
	5 to 45	65 to 98	Full Scale
	10	80 to 85	Laboratory Units at 20°C
	10	25	Laboratory Units at 5°C
	up to 110	essentially total	Laboratory Units
	2.2 to 5.1	11 to 96	Range of averages for monthly data for 6-month period from 7 Canadian Cities. Average removal = 72 percent.
	up to 8	90	Full scale
	16	75	Full scale

*Possibly unacclimatized

of NTA to primary tank effluent and allowing a few minutes contact time achieved 25% and 36% removal respectively, indicating that NTA could be bound by sludge solids and hence removed. They concluded that the mechanism of removal was solids adsorption and that this mechanism was a significant factor in the removal of NTA in sewage treatment.

In contrast to investigation into NTA removal in primary sedimentation, NTA removal in aerobic treatment has been widely studied at laboratory scale, and in the field. Thompson and Duthie (1968), using synthetic sewage containing NTA at a concentration of $30 \text{ mg } \ell^{-1}$ supplied continuously, found greater than 90% removal after periods of up to 21 days acclimatization. Pfeil and Lee (1968) under similar conditions but using real sewage and a NTA dosage progressively increasing from $10 \text{ mg } \ell^{-1}$ to $100 \text{ mg } \ell^{-1}$ achieved almost complete removal after 7 days acclimatization. In these tests it was found that 5 days without any NTA dose required a further 2 days acclimatization when dosing was recommenced. Swisher et al., (1967) used NTA concentrations progressively increasing from $80 \text{ mg } \ell^{-1}$ to $500 \text{ mg } \ell^{-1}$ and found greater than 90% removal after 2 to 3 weeks acclimatization. The experiments were conducted with synthetic sewage, but the plant was initially seeded with activated sludge from a municipal treatment plant.

Eden et al., (1972) investigated the effect of temperature on NTA removal using real sewage containing NTA concentrations varying from 5 to $20 \text{ mg } \ell^{-1}$. At 5°C removal was only about 3% after 40 days, but on raising the temperature to 20°C after a 14 days acclimatization period, removal reached 95% with a consistent 98% after 21 days. Dropping the temperature to 7.5°C reduced the removal efficiency to between 66% and 82%, but a further rise to 10°C improved it again to about 95%. They concluded that in the U K removal would be very good under summer conditions but would be greatly reduced in winter. Shannon et al., (1978) found a similar temperature dependence on biodegradation although for temperatures between 10°C and 15°C and for initial NTA concentration of $10 \text{ mg } \ell^{-1}$ (as H_3NTA) they suggested removal efficiencies in the order of 50%. Bouveng et al., (1968) using real sewage confirmed temperature dependence with 80% to 85% removal at 20°C and 25% removal at 5°C . They also investigated the adsorption of NTA onto activated sludge flocs and concluded that up to 25% of the influent dose might be removed by this mechanism. This would suggest that a substantial proportion of NTA removal in biological treatment is not biodegradation as most investigators have assumed but is physical transfer to the sludge.

Numerous studies have been carried out to examine the effects of NTA on the performance of activated sludge sewage treatment plants. Thompson and Duthie (1968) studied the effect at laboratory scale and using synthetic sewage with various concentrations of NTA. They discovered no variation in the settleability of activated or primary sludges for 1 to 50 mg ℓ^{-1} NTA, nor did they find any variation in SVI. In tests where between 5 and 90 mg ℓ^{-1} were added to laboratory scale digesters, no effects on pH or gas production were observed. Moore and Barth (1976), in a similar experiment dosing 20 mg ℓ^{-1} to digesters over a period of 3 months (after 1 month with no NTA), noticed no change in organic loading, gas production or volatile solids destruction. Swisher et al., (1967) conducted experiments using synthetic sewage on a laboratory scale plant seeded with activated sludge from a municipal treatment plant. For various concentrations of NTA up to 500 mg ℓ^{-1} there was no effect on sludge settlement and negligible effect on the removal of COD or anionic surfactants. In another laboratory scale test, Eden et al., (1972) found no effect on BOD or COD removal for concentrations up to 20 mg ℓ^{-1} and in a field study, Shumate et al., (1970) after dosing NTA incrementally up to 16 mg ℓ^{-1} into a domestic sewage treatment plant noticed no effects on the plant's performance. Shannon (1975) concluded the same when detergent containing NTA was distributed in a small community and its effect checked in the local sewage treatment.

The effect of NTA on phosphorus removal was studied by Bouveng et al., (1968) and Shannon (1975) both at laboratory scale. The former concluded that NTA chelates the aluminium ion more strongly than the calcium, resulting in more chemical being required for phosphorus removal. The latter, however, found that NTA did not interfere in phosphorus treatment by complexing the iron, aluminium or calcium ions, nor by forming a NTA-phosphate-metal complex. In fact, less coagulant chemical was required when NTA was present than when it was not.

Full-scale investigations of NTA removal in aerobic treatment have been conducted by Renn (1974) and by Shumate et al., (1970). Renn (1974) distributed NTA-built detergent to an isolated community of 150 mobile homes and then monitored the extended aeration treatment plant serving the community. Influent NTA concentrations were between 40 and 50 mg ℓ^{-1} and over the first 3 months (spring and summer) less than 20% removal was achieved. When the detergent had been used up,

he dosed NTA to the plant influent in increasing concentrations from $5 \text{ mg } \ell^{-1}$ to $20 \text{ mg } \ell^{-1}$ over the following four months. NTA removal efficiency almost immediately increased to 80% and then progressively increased to a maximum of 98% towards the end of the 4 month period. During the winter months that followed, with mixed liquor temperatures of 9°C to 11°C and a NTA concentration of $30 \text{ mg } \ell^{-1}$, the removal efficiency dropped to about 80%. Shumate et al., (1970) conducted a similar study, but dosed NTA at 8 to $16 \text{ mg } \ell^{-1}$ only between 8.00 a.m. and 10.00 p.m. each day for an 8 month period.. At $8 \text{ mg } \ell^{-1}$ there was 90% removal of NTA, but at $16 \text{ mg } \ell^{-1}$ only 75% on average with a wide variation in results.

Björndal et al., (1972) and Stoveland et al., (1979a) both showed the dependence of NTA removal on water hardness. The former using real sewage found significantly better biodegradation in hard water than soft. The latter found that NTA removal reached 83% to 100% after 16 to 31 days acclimatization for a hard water synthetic sewage, but no biodegradation was achieved after 60 days for soft water synthetic sewage. The influent NTA concentration was $10 \text{ mg } \ell^{-1}$ (as NTA^{3-}).

The chelating ability of NTA has necessitated studies of the removal of various NTA-metal complexes in biological sewage treatment (Shannon, 1975; Shannon et al., 1978; Björndal et al., 1972). The studies showed that some NTA-metal complexes degraded more readily than others, and some did not degrade at all. Shannon (1975) and Shannon et al., (1978) concluded that NTA complexes with cadmium, nickel and mercury were resistant to biodegradation, the latter possibly due to metal toxicity, while complexes with calcium, iron, aluminium, lead, chromium, copper and zinc readily degraded. Björndal et al., (1972), in tests on copper, nickel and cadmium, agreed that nickel was resistant to degradation and copper was not, but found that there was extensive biodegradation of the cadmium complex. Warren (1974) in his review of the biodegradability of NTA-metal complexes, stated that calcium, magnesium, sodium, manganese, iron and lead complexes biodegrade rapidly, while mercury, cadmium, copper, nickel and zinc are resistant.

Waste water treatment processes have assumed an important role in the hydrological cycle with an increasing tendency towards water re-use. In particular, their capacity for the removal of heavy metals is important, since significant concentrations of heavy metals in

waste water treatment effluents may cause substantial pollution of receiving waters, possibly leading to the infringement of standards for their concentrations in water to be abstracted for drinking water or in potable supplies. In table 4 international drinking water quality criteria for trace metals are summarised.

Table 4 - Drinking water quality criteria for trace metals*

	USPHS (1962)	Japan (1968)	USSR (1970)	WHO Euro- pean (1970)	WHO Intern. (1971)	SABS (1971)	NAS (1972)	Aust- ralia (1973)	US EPA (1975)	FRG (1975)
Arsenic	10	50	50	50	50	50	100	50	50	40
Barium	1,000	-	4,000	1,000	-	-	1,000	1,000	1,000	-
Cadmium	10	-	10	10	10	50	10	10	10	6
Chromium	50	50	100	50	-	50	50	50	50	50
Copper	1,000	10,000	100	50	50	1,000	1,000	10,000	-	-
Lead	50	100	100	100	100	50	50	50	50	40
Mercury	-	1	5	-	1	-	2	-	2	4
Selenium	10	-	1	10	10	-	10	10	10	8
Silver	50	-	-	-	-	-	-	50	50	-
Zinc	5,000	100	1,000	5,000	5,000	5,000	5,000	5,000	-	2,000

*As proposed by the World Health Organization (WHO), US Public Health Service (USPHS), South African Bureau of Standards (SABS), Russia (USSR), USA National Academy of Sciences (NAS), Australia, Japan and Environmental Protection Agency (EPA) of the USA. All concentrations in $\mu\text{g } \ell^{-1}$. Compiled by Hattingh (1977), except for Federal Republic of Germany (F.R.G.) data (Schöttler, 1977).

Cadmium, chromium, copper, lead, nickel and zinc are probably, with the exception of mercury, the most significant heavy metals in terms of environment health. Their health effects are summarized in Table 5.

Metal removal may occur during waste water treatment in two distinct phases (Oliver and Cosgrove, 1974). Removal during primary sedimentation is a physical process, dependant on the association of metals with settleable particulate matter, while removal in secondary biological treatment is probably a more complex process, dependant on a variety of factors (Brown and Lester, 1979).

Table 5 - Significance of some heavy metals to human health

Metal	Effect
Cd	Toxic; causes hypertension, cardiovascular problems; accumulates in kidney, liver and reproductive organs; Itai Itai disease; increase of risk of prostate and respiratory tract cancer (World Health Organisation, 1977).
Cr	Essential for normal metabolism of glucose; Cr(VI) more toxic than Cr(III) compounds; causes ulceration, respiratory disease; potential carcinogenic effect (Association Européenne Oceanique, 1977).
Cu	Essential in trace amounts, involved in a number of enzymes (Dulka and Risby, 1976); chronic excess will lead to anemia with accompanying hepatic and renal necrosis (Buck, 1978).
Pb	Toxic; metabolism similar to Ca; accumulates in bones and soft tissues, particularly in the brain; complexes with -SH groups; causes anaemia; produce subclinical effects involving mental retardation, hyperactivity and other forms of neurological impairment (Lee, 1972; Green <u>et al.</u> , 1978).
Ni	Essential; involved in enzyme activity, hormonal action; causes dermatitis, respiratory disorders; potential carcinogenic effect; environmental and occupational exposure to nickel has been associated with hepatic cirrhosis and chronic renal insufficiency (Shamberger, 1978; Zingaro, 1979).
Zn	Essential, present in some enzymes and metalloproteins; large amounts cause vomiting, diarrhoea; required for skin repair (Farnsworth and Kline, 1973).

Lester et al., (1979) and Stoveland et al., (1979e) found removal efficiencies for cadmium, chromium, copper, lead and zinc in primary sedimentation of 70% or greater, although the mean nickel removal

efficiency was only 23%. Similar removal efficiencies for these metals were observed by Oliver and Cosgrove (1974) in short term (3 days) and long term (4 weeks) studies. Removals were typically greater than 50%, the exceptions being copper (30-33%) and nickel (15-19%). In addition, Oliver and Cosgrove (1974) found removals of iron, manganese and mercury of 36-49%, 32-33% and 60% respectively. In a less intensive study, removals of cadmium, copper and lead of 43%, 61% and 67% respectively have been determined by Lewin and Rowell (1973). Several authors have frequently encountered heavy metal removals in primary sedimentation of greater than 50%, indicating the potential of the process for efficient metal removal. Brown et al., (1973) found copper, lead and zinc removals of about 60-70%, but in contrast, cadmium and chromium removals were poor. Relatively low heavy metal removal efficiencies have been reported by some authors. In studies undertaken by Stones (1955, 1958, 1959a, 1959b, 1960) the removals of chromium, copper, lead, nickel and zinc did not exceed 45%, while Roberts et al., (1977) found that the removals of these metals, plus cadmium, were in the range of 30% - 50%. As in other studies, nickel removal efficiency was at the lower end of this range, but in contrast to the results obtained by other workers, cadmium and zinc removals were comparably poor. Davis and Jacknow (1975) presented data for mean influent and primary effluent concentrations of heavy metals over a period of six months at a full scale treatment plant. These data indicate that nickel removal was only 1-2% and that removals of cadmium, chromium, copper and zinc were less than 25%. Only lead was removed with an efficiency of greater than 50%. The range of heavy metal removal efficiencies is reported in Table 6 .

Considerable variations in influent heavy metal loading and heavy metal concentration to primary sedimentation tanks were observed by Roberts et al., (1977). Concentrations of heavy metals in the raw sewage were typically 3-5 times higher during the day than during the night, corresponding to a day time to night time load of between 5:1 and 8:1. Higher influent flows of raw sewage caused by urban run-off may be associated with disproportionately high metal loadings. In one instance, lead showed a peak load of 30 times the normal load occurring in dry weather conditions. The poor metal removal efficiencies observed by Roberts et al., (1977) in comparison to

Table 6 - Heavy metal concentrations in raw sewage and their removals in primary sedimentation process

Reference	1		2		3		4		5 & 6		7		8	
Metal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal	conc $\mu\text{g}\ell^{-1}$	% Removal
Cadmium	24	25	-	-	6	60	5	30	6	72	7	43	21	14
Chromium	190	36	710	28	290	55	90	40	60	51	-	-	95	17
Copper	220	70	560	45	310	33	120	40	160	70	430	61	127	23
Lead	390	59	620	40	230	66	140	50	160	73	630	67	119	54
Nickel	-	-	190	21	330	15	80	35	40	23	-	-	78	1
Zinc	1050	68	910	41	2400	54	600	35	1650	74	-	-	418	19

1. Brown et al., (1973)
2. Stones (1977)
3. Oliver and Cosgrove (1974)
4. Roberts et al., (1977)

5. Lester et al., (1979)
6. Stoveland et al., (1979e)
7. Lewin and Rowell (1973)
8. Davies and Jacknow (1975)

other workers may have been due to large variations in loading. However, Oliver and Cosgrove (1974) found 8-10 fold variations in the concentrations of some heavy metals in influent raw sewage over periods of less than six hours, but reported that removal efficiencies were fairly consistent throughout a longer period of study. Stoveland et al., (1979e) collected 24h composite samples on four separate occasions and found that the removal of nickel exhibited considerable variations (0-40%) despite the fact that the daily loading of nickel was the least variable of all the metals studied.

Heavy metal removal in primary sedimentation depends upon the presence of the metal in a settleable or potentially settleable form. Metals which are removed may exist in insoluble forms or forms which have the capacity for binding to settleable solids. Thus the speciation of heavy metals in the influent sewage may influence their removals. Jan and Young (1978) demonstrated that the dominant dissolved species of chromium in raw sewage was the trivalent form and that about 60% of the chromium was in a particulate state. Bailey et al., (1970) showed that trivalent chromium was largely removed in sedimentation, leaving the hexavalent species in solution. Chen et al., (1974) studied particle size distributions of heavy metals in primary effluent. It was found that most of the cadmium, chromium, copper, iron, mercury and zinc was associated with particulates, while nickel, lead and manganese were predominantly soluble. Approximately 50% of the metals in a predominantly particulate form were associated with particles less than 8 μm in diameter. This suggests that the optimum removal of most metals may be dependant on the efficient sedimentation of smaller particles, while the data on nickel, lead and manganese may indicate that the optimisation of suspended solids removal would have a lesser effect on their removals.

Further metal removal occurs in the activated sludge process (secondary biological treatment) by the adsorption on to the sludge flocs of dissolved metals or fine particulate metals (Oliver and Cosgrove, 1974; Brown et al., 1973). Some authors (Brown et al., 1973; McDermott et al., 1962; 1965; Chen et al., 1974) report that activated sludge is more efficient at removing metals than primary settling. Brown et al., (1973) found that chromium, copper and lead were removed more efficiently from waste water in secondary treatment plants than in the primary treatment process. The average removal percentage of zinc, however, was comparable at both stages of treatment. The removal efficiencies of a range of metals by

activated sludge treatment plants, activated sludge pilot plant and laboratory scale activated sludge units are summarised in Table 7. The wide range of removal efficiencies observed for any one metal demonstrates the variability of conditions prevailing in an activated sludge plant. It is apparent that metal removal efficiencies may be extremely high on occasion. It appears from the results presented that copper, chromium and zinc have the highest metal removal efficiencies and nickel the lowest average removal efficiency.

The relationship between metal concentration in solution and metal uptake by activated sludge flocs has been investigated, and it appears that this may differ with different metals. A relationship between heavy metal loading and heavy metal removal was found for chromium, copper, lead, zinc and cadmium in a study of six treatment plants (Brown *et al.*, 1973). Over the range of loadings studied ($< 2,000 \mu\text{g l}^{-1}$), the percentage heavy metal removal was directly proportional to the initial metal loadings. This relationship has been identified by several other workers (Neufeld and Hermann, 1975; Cheng, 1974; Forster, 1976), and fitted to Langmuir and Freundlich isotherms.

Further investigations into the time course of metal uptake in activated sludge have revealed that this process occurs in two stages. Cheng *et al.*, (1975) have proposed a two-step reaction model for metal uptake. The first stage is a rapid uptake phase of between 3 and 10 min, in which a large quantity of metal ions are adsorbed by the cell flocs. The second is a slow phase which may extend over many hours. Neufeld and Hermann (1975) found that after 3 h, the system had approached almost complete equilibrium for mercury, cadmium and zinc, but 2 weeks were required for complete equilibrium to be achieved. Rudolfs and Zuber (1953) also identified a rapid metal removal phase occurring in the first 30 to 60 min.

Many different factors have been shown to affect the removal of metals in the activated sludge process. These may be divided into plant operating parameters, physical or chemical factors and biological factors (Brown and Lester, 1979). Operating parameters which have been shown to affect metal removal are sludge volume index, sludge age, suspended solids removal, dissolved oxygen concentration and settling time. Physical and chemical factors affecting

Table 7: Heavy metal concentrations in settled sewage and their removals in activated sludge process

Reference	1 *		2 *		3 & 4 *		5 *		6 *		7 *		8 **		9 **		10 ***		11 ***	
Metal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal	conc $\mu\text{g l}^{-1}$	% Removal
Cadmium	3	50	3	7	2	33	18	11	19	47	-	-	18	62	13	39	10	26	9	69
Chromium	130	54	50	50	30	33	59	78	310	82	270	69	79	60	210	57	100	88	95	95
Copper	210	60	72	25	40	86	170	61	110	77	480	83	98	43	920	33	100	35	180	42
Lead	90	79	70	30	40	78	160	43	100	53	380	92	55	61	95	56	100	27	70	47
Nickel	280	1	50	15	30	61	-	-	190	41	110	32	77	9	73	21	100	14	110	25
Zinc	1130	50	390	38	420	78	350	48	310	59	3590	57	530	57	320	65	500	49	610	51

* Full-scale treatment

** Pilot Plant

*** Laboratory scale
(synthetic sewage)

1. Oliver and Cosgrove (1974)

2. Roberts et al., (1977)

3. Lester et al., (1979)

4. Stoveland et al., (1979e)

5. Brown et al., (1973)

6. Chen et al., (1974)

7. Stones (1977)

8. Davis and Jacknow (1975)

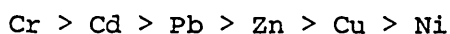
9. Esmond and Petrasek (1974)

10. Stoveland et al., (1979a)

11. Sterritt and Lester (1980)

metal removal are temperature, pH, metal ion concentration, metal solubility, metal valency, concentration of complexing agents and particle size. The main biological factor, which does not qualify as an operating parameter, is the concentration of bacterial extra-cellular polymers (Brown and Lester, 1979).

Rudolfs and Zuber (1953) found that as the SVI increased in activated sludge, the removal capacity for metal decreased. Higher heavy metal removals have been observed at higher sludge ages, particularly for lead and zinc, (Stoveland and Lester, 1980). Using synthetic sewage and metals added at typical influent concentration Sterritt and Lester (1980) found that activated sludge simulations operating under stable conditions achieved optimum heavy metal removal at sludge ages between 9 and 15 d. These authors suggested the following series of decreasing order of affinity of the metals for the biomass:



As the suspended solids removal increased, metal removal was shown to increase at an exponential rate (Brown et al., 1973). It has been proposed (Chen et al., 1974; Brown et al., 1973) that the greater efficiency of the activated sludge process in metal removal is due to the greater suspended solids removal in an activated sludge plant than in primary treatment. Barth et al., (1965) found the amount of removal of copper, zinc, nickel and chromium was controlled by the concentration of dissolved oxygen present. Lead was found to be removed more efficiently due to the increased settling time in secondary treatment in comparison with primary treatment (Brown et al., 1973).

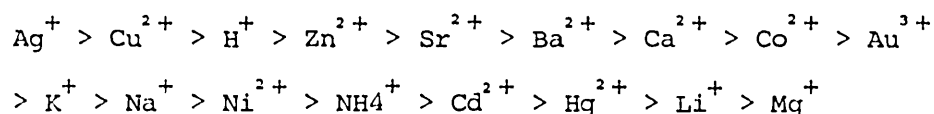
Stumm and Bilinski (1973) have summarised the forms of metals occurring in natural waters as: free metal ions, inorganic complexes, organic complexes (chelates), bound to higher molecular weight organic material, highly dispersed colloids, sorbed on colloids and precipitates on organic particles. At a high pH, considerable precipitation of metal hydroxides occurs, while at low pH there is much interaction between metals and organics (Cheng et al., 1975). Several workers have observed that metals passing through a sewage treatment works may be in a soluble or precipitated form. Oliver and Cosgrove (1974) discovered that much of the lead and iron in waste water was converted

into an insoluble form on reacting with municipal sewage; these metals were very efficiently removed. They observed that for most metals the proportion of dissolved to total metal increased as metals passed through the treatment process. However, they found no proportionate removal or equilibrium between the soluble and insoluble states of a metal. Brown et al., (1973) found low cadmium removal efficiencies in sewage treatment plants, and proposed that this was due in part to the high solubility of cadmium ions at pH 7 to 9 (the normal pH of sewage treatment processes) and to the greater availability of other more concentrated metals which form stable, insoluble complexes with sewage sludges. In the case of chromium, the oxidation state or valency has been found to affect removal efficiency. Although chromium normally enters the treatment plant in the hexavalent form (Moore et al., 1961), it has been demonstrated (Brown et al., 1973) that during aeration it may be reduced to the trivalent form. Stoveland (1978) has shown that the removal efficiency for trivalent chromium in modified Hussman's activated sludge units was typically between 70 and 90%. while hexavalent chromium removal efficiency was typically approximately 20%. It appears that conversion of hexavalent chromium into trivalent chromium is desirable in the activated sludge process.

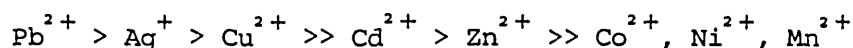
Several strong complexing or chelating agents may be present in waste water. EDTA has many industrial uses (Mark et al., 1965). Nitritotriacetic acid and sodium tripolyphosphate are used as detergent builders (Stoveland et al., 1979c). Fulvic and humic acids are natural chelators which may also be present in waste water (DeWalle and Chian, 1974; Schnitzer and Khan, 1972). In addition to chelating substances ion-exchangers such as zeolite type A may be present as a consequence of their use in detergents (Hopping, 1978). Both ion exchange and chelating compounds may influence metal removal during waste water treatment depending on their own removal (absorption to sludge solids) or degradation (Berth, 1978; Stoveland et al., 1979c; Thom, 1971). Zeolite type A is not amenable to biological degradation. Its influence upon heavy metal removal during sewage treatment is essentially dependent on its affinity for the elements and the efficiency of its removal during sedimentation.

The thermodynamic behaviour of zeolite type A has been studied and exchange isotherms with metals have been reported (Breck, 1974); the selectivities for cations have been placed in the following

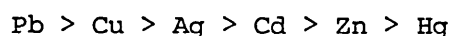
order (Schwuger et al., 1976):



which generally agrees with the selectivities for divalent ions reported elsewhere (Breck et al., 1956); these authors indicated that the exchange of sodium for Ba^{2+} , Cu^{2+} and Fe^{3+} destroyed the zeolite structure. Since the ion exchange reactions are kinetically controlled these thermodynamic selectivities may be of secondary relevance and it is the selectivities at the low concentrations of metal found in the environment that are important. The order of selectivities at low environmental concentrations of ionic metal has been reported (Schwuger et al., 1976) as:



The ion exchange has also been reported (Schwuger et al., 1976) to increase with decreasing water hardness, increasing temperature, increase in the pH of the solution, increasing concentration of aluminium silicate and decreasing concentration of heavy metals. At a concentration of the sodium form of zeolite of 100 mg l^{-1} and 1 mg l^{-1} each of lead, silver, copper, cadmium and zinc in a solution of hardness 110 mg Ca l^{-1} at 23°C and pH 7 only lead and silver were completely removed after one hour; after 24 h, 50% of the copper, 25% of the calcium and 10% of the zinc were removed (Schwuger et al., 1976). Berth (1978) indicates that the uptake of heavy metals in sewage is slight and that there is minimal mobilization; the order of uptake reported was:



Studying the effect of zeolite on metal removal during sedimentation in settling column tests, Obeng et al., (1981) concluded that the addition of zeolite within the range of its expected concentration in sewage, would neither enhance nor adversely affect to any significant degree the removal of metals during primary sedimentation. However, it was suggested that longer contact times typical of full scale process in conjunction with the lower concentration of zeolite used might lead to an improvement in the removal of some metals in the absence of other chelating agents.

The influence of zeolite type A on heavy metal transfer in activated sludge process has been studied by Carrondo (1979), Stoveland et al., (1980a) and Obeng et al., (1980). Carrondo (1979), using an activated sludge pilot plant and zeolite type A dosed at 15 and 30 mg l^{-1} and 25% calcium exchanged, found no effect on cadmium, chromium, nickel and lead removal. The zinc results were inconclusive and there appeared to be a slight improvement in the removal of copper. Stoveland et al., (1980a), using a laboratory scale plant with synthetic sewage reported the effect of zeolite on the removal of zinc and copper in experiments at constant loading. When a shock loading was imposed, these authors found slight reductions in the removal of chromium, copper, lead and zinc. Obeng et al., (1980), working with synthetic sewage in laboratory scale plant concluded that zeolite did not adversely affect metal removal and suggested that it could slightly improve removal of lead and to a lesser extent zinc and cadmium.

As the removal of NTA during primary sedimentation is substantially incomplete its biodegradation during aerobic biological sewage treatment will be critical in determining effluent concentrations of heavy metals (Stoveland et al., 1979a and 1979b).

The ability of NTA to solubilise metals is well established. It was demonstrated by Gudernatsch (1970) that copper was changed from an insoluble to completely soluble form by the addition of 25 mg l^{-1} NTA in a solution containing from 2 to 10 mg l^{-1} of heavy metals, 25 mg l^{-1} of disodium hydrogen orthophosphate and at pH values between 7 and 8. Similarly lead, which was initially totally insoluble, was solubilised by 50%. Metal mobilization from river sediments was studied by Banat et al., (1974). They found substantial solubilisation of cadmium and copper by NTA. In similar experiments using a standardised water medium with a hardness of approximately 260 mg l^{-1} (as CaCO_3) Dietz et al., (1975) found the order of solubilisation to be:



These results support data presented by Gregor (1972). He found that insoluble lead deposits, from automobile exhausts, in lake sediments could be substantially resolubilised by concentrations

of NTA between 2 and 20 $\text{mg}\ell^{-1}$. The concentration of soluble lead in the lake water as a consequence would have been much higher than that allowed by the United States Public Health Service drinking water standards (see Table 4). There is little information indicating the resolubilisation of heavy metals from biological sewage sludge. However, the uptake of nickel by activated sludge was found to increase as the concentration of NTA present decreased (Cheng *et al.*, 1975). These results indicated that the affinity of the metal ions for the biological solids was much less than that for strong chelating agents such as NTA.

In a simulated activated sludge unit acclimated to NTA where the influent NTA concentration was kept constant at 10 $\text{mg}\ell^{-1}$ (as NTA^{3-}), the overall percentage heavy metal removal was found by Stoveland *et al.*, (1979a) to be 5% less than a builder free control and 20% less than a phosphate system. Reduction in the removal efficiencies for nickel, copper and zinc were observed, presumably the effect of a small quantity of NTA which was not biodegraded. Results obtained under such conditions only indicate some of the effects which may occur in a full-scale activated sludge treatment works, since all the constituents of the influent were kept constant throughout the experiments. In a field situation, this would not be so, since both the organic, heavy metal and NTA loadings would exhibit daily, weekly or even seasonal variations. The pattern of NTA variations in the influent sewage would be very much dependent on the washing routine and the size of the community which the sewage treatment works was serving.

Considerable variations in the NTA concentration of sewage were found by Shannon and Kamp (1973) during a detergent substitution study at an army camp in Canada. A maximum concentration of 14 $\text{mg}\ell^{-1}$ NTA was recorded on a Thursday, while the weekly average measured by means of 4 h composite samples was 2 $\text{mg}\ell^{-1}$. Under these conditions an average of only 60% of the NTA was biodegraded. Work presented by Rudd (1974) indicated that the micro-organisms responsible for NTA biodegradation required some time to adapt to increasing NTA concentrations. An increase in the influent concentration of NTA from 5 to 10 $\text{mg}\ell^{-1}$ caused a temporary increase in the effluent NTA concentration. Removal of NTA was reduced from 90 to 65% before

recovering steadily to its original value. This period of steady improvement probably corresponded to the time required for the micro-organisms to adapt to the higher influent concentration of NTA. As a consequence, NTA would have escaped into the receiving waters and associated with it a proportion of the metallic content of the influent sewage. This is consistent with the observations of Renn (1974), who found that when NTA was introduced into a sewage treatment works, unacclimatized to NTA, zinc and iron removal efficiencies were reduced from 75% and 80% respectively to approximately zero. Later when NTA biodegradation had commenced, the effluent zinc concentration decreased again, while the concentration of iron in the effluent was variable and frequently in excess of the concentrations in the influent. Copper removal efficiencies did not appear to be affected by NTA in this study.

The biodegradation of NTA was reported by Bouveng *et al.*, (1968) to be inferior to BOD removal, as a consequence of its higher sensitivity to operational disturbances. When dosing NTA at 25 mg l^{-1} in a full scale activated sludge plant treating mixed industrial and domestic sewage, Gudernatsch (1974) demonstrated that the ranges and standard deviations for the biodegradation of the NTA-metal complexes were much greater than those for BOD removal. In these experiments metals including cadmium, copper, nickel and zinc were dosed individually at concentrations sufficient to achieve a 1:1 NTA-metal complex. The standard deviations for the biodegradation of the NTA-copper complex and NTA-zinc complex were twice those of the BOD removal.

It is evident that the behaviour of detergent builders during waste water treatment may have a significant effect on their own removal and possibly on effluent heavy metal concentrations. This is of concern where these effluents are discharged to surface waters which may be abstracted as sources of potable supply.

2 OBJECTIVES

The behaviour of detergent builders during waste water treatment processes has in general been the subject of limited studies, in particular the removal of zeolite type A and NTA during primary sedimentation has received limited attention as have their effects on heavy metal removal in that process. It was intended in the work reported here to:

1. Establish the degree of heavy metal removal which occurs in the absence of zeolite type A or NTA during primary sedimentation at constant and varying hydraulic conditions.
2. Determine the removal of zeolite type A and NTA during primary sedimentation at constant and variable hydraulic conditions.
3. Assess the effect of zeolite type A and NTA on metal removal during primary sedimentation under constant and variable hydraulic conditions.

The literature on the behaviour of zeolite type A in biological treatment has shown that it has no adverse effects on the process and it is not amenable to biological degradation. However, NTA is biodegradable and could interfere in the process of metal removal because of its capacity to sequester metallic ions since its removal is unreliable during biological sewage treatment. Whilst information about biodegradation of NTA is considerable, and it is known that operational parameters influence its biodegradation, its effect on heavy metal removal has received only modest attention, in particular shock loading of NTA into the activated sludge process has not been investigated. Therefore the following were considered worthy of investigation:

1. An evaluation of the degree of heavy metal removal which occurs in the activated sludge process in the absence of NTA at different sludge ages and at different influent heavy metal concentrations.
2. Effects of shock loads of NTA on its biodegradation in the activated sludge process at different sludge ages and different influent heavy metal concentrations.
3. The removal of heavy metals in activated sludge in the presence of NTA during shock loading at different sludge ages and different influent heavy metal concentrations.

3. MATERIALS AND METHODS

3.1 Primary Sedimentation Pilot Plant

3.1.1 Design criteria

The primary sedimentation pilot plant was designed using the parameters normally applied to the design of a full scale plant. The two parameters considered to be of greatest importance were surface loading and retention time. Modern practice suggests values of 1.4 to 1.7 m h⁻¹ for surface loading when treating domestic wastewater to obtain 50 to 60% suspended solids removal from the average 24 h flow (Water Pollution Control Federation, 1977). However, more conservative values of 1.5 to 2.0 m h⁻¹ for 3 DWF were used by CIRIA (Sidwick, 1977) during a study of the rationalisation of circular sedimentation tanks. Metcalf and Eddy (1974) stated that "normally, primary sedimentation tanks are designed to provide 90 to 150 min of detention time based on the average rate of flow" and that shorter periods of 30 to 60 min are used frequently for preliminary treatment ahead of biological treatment units.

Since heavy metal determinations were to be made on samples from the pilot plant it was necessary to minimise errors resulting from adsorption or leaching of metals; the tanks used were therefore constructed of plastic material. Standard fibre glass humus tanks (K.T.S. Construction Co. Ltd., Tamworth, U.K.) were used. A test on a specimen of the fibre glass used in the construction of these tanks indicated that metals were not mobilised from this material by NTA in the concentration expected in sewage (Appendix VII). Since detergent builders were dosed the smallest size was chosen to minimise the quantity of builder required, this also made the construction and transport of these units easier. The surface area and the volume of the tanks were determined by the manufacturer thus the relation between flow and surface loading was also fixed. The conditions presented in Table 8 were used during the experiments reported here; these satisfy the design parameters previously cited.

Table 8 - Values for flow, surface load and retention time for the pilot plant when operated under various conditions

Conditions	Flow l s ⁻¹	Surface load m h ⁻¹	Retention time h
1 DWF	0.111	0.56	2.29
3 DWF	0.333	1.68	0.76
Variable flow	0.045-0.168	0.23-0.85	-

Since the tanks had a 60° hopper no attempt was made to use a scraper to aid sludge removal. As the level is important in this kind of installation the framework which supported the tanks was designed to be adjustable "in situ".

3.1.2 Description

3.1.2.1 - General description

The plant consisted of nine unit systems: sewage intake, constant head loading and distribution system, rapid mixing system, sedimentation tanks, flow measuring system, sludge discharge, dosing system, sampling system, electrical and timer control panel. It had two identical sedimentation tanks, one acting as the control to the other (the test). Raw sewage was drawn from the same source and equally distributed to both tanks. A pictorial flow diagram is presented in Fig. 1 and Plates 1 to 8 show the various components of the pilot plant.

3.1.2.2 - Sewage intake

The intake system was located at the distribution chamber of the primary settlers of the Hogsmill Valley Works. The sewage had already been subjected to preliminary treatment by constant velocity grit channels and comminution. The sewage passed into a cylindrical stainless steel drum (60 cm diameter and 90 cm in height), which contained a submergible pump. The base of the drum was covered by a stainless steel screen (plain weave, 6 mesh), this proved to be too efficient, therefore four rows of circular holes (19.05 mm diameter and 38.1 mm between centres) were drilled around the base to permit the entry of sewage. The pump, Turo type T1-32 UM2 (Moffat and Bell Ltd., Surrey, U.K.) had a capacity of 3.17 ls^{-1} at a head of 6 mlc and delivered the sewage through a 38 mm wide ABS pipe (Durapipe Ltd., London, U.K.). The hydraulic loading could be adjusted by an ABS ball valve, which discharged the surplus flow via a pipe. The pump and the drum were lifted upward by a pulley system for regular cleaning. Plate 1 is a view of the system.

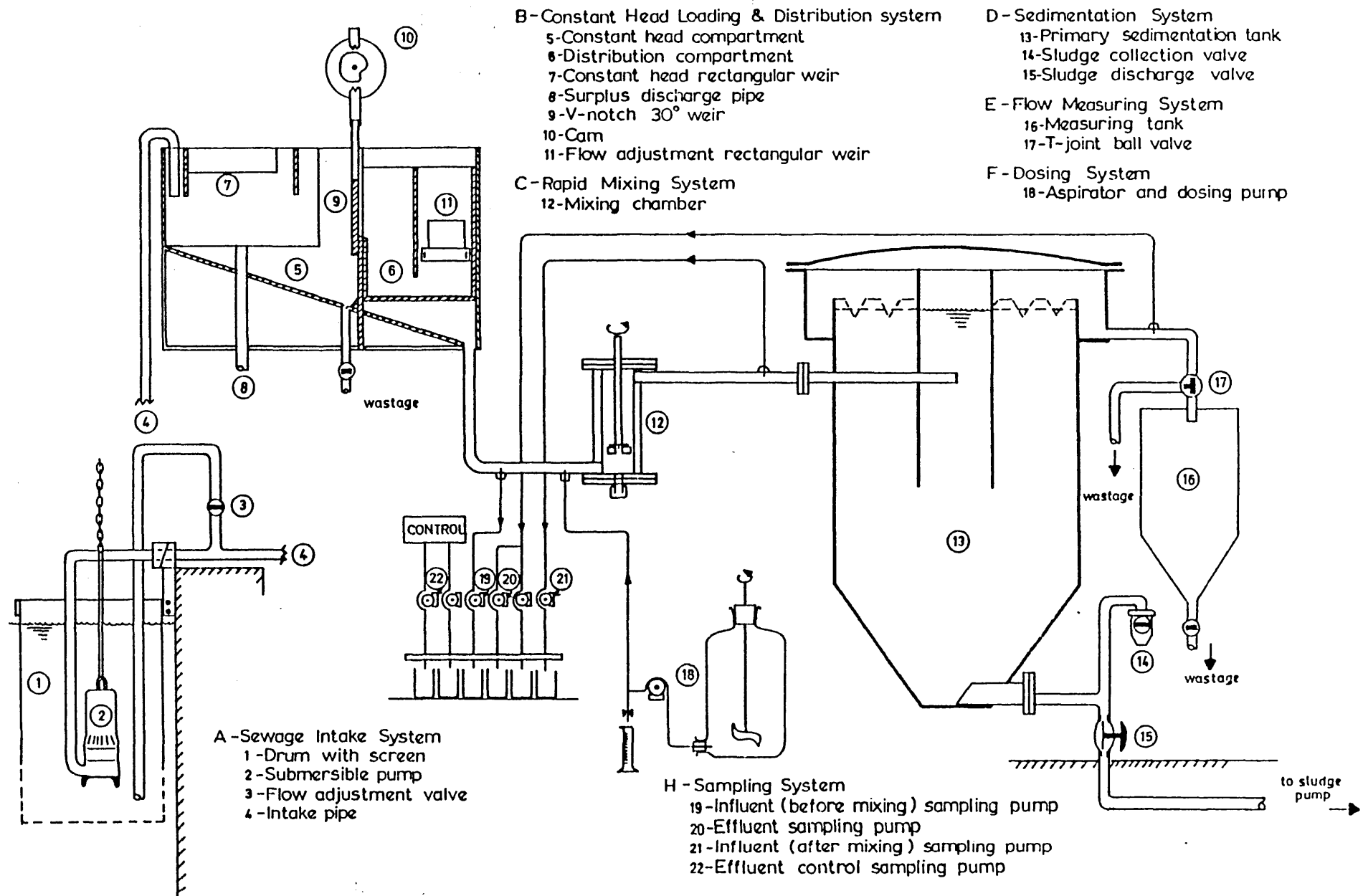


Figure 1- Pictorial flow diagram of the primary sedimentation pilot plant



Plate 1 - Intake system for Primary Sedimentation Pilot Plant
including the submergible pump, screen and hoist.



Plate 2 - General view of the Primary Sedimentation Pilot Plant.



Plate 3 - Constant head loading and distribution system for the
Primary Sedimentation Pilot Plant.



Plate 4 - Programmable flow simulator and movable weir for the
Primary Sedimentation Pilot Plant.

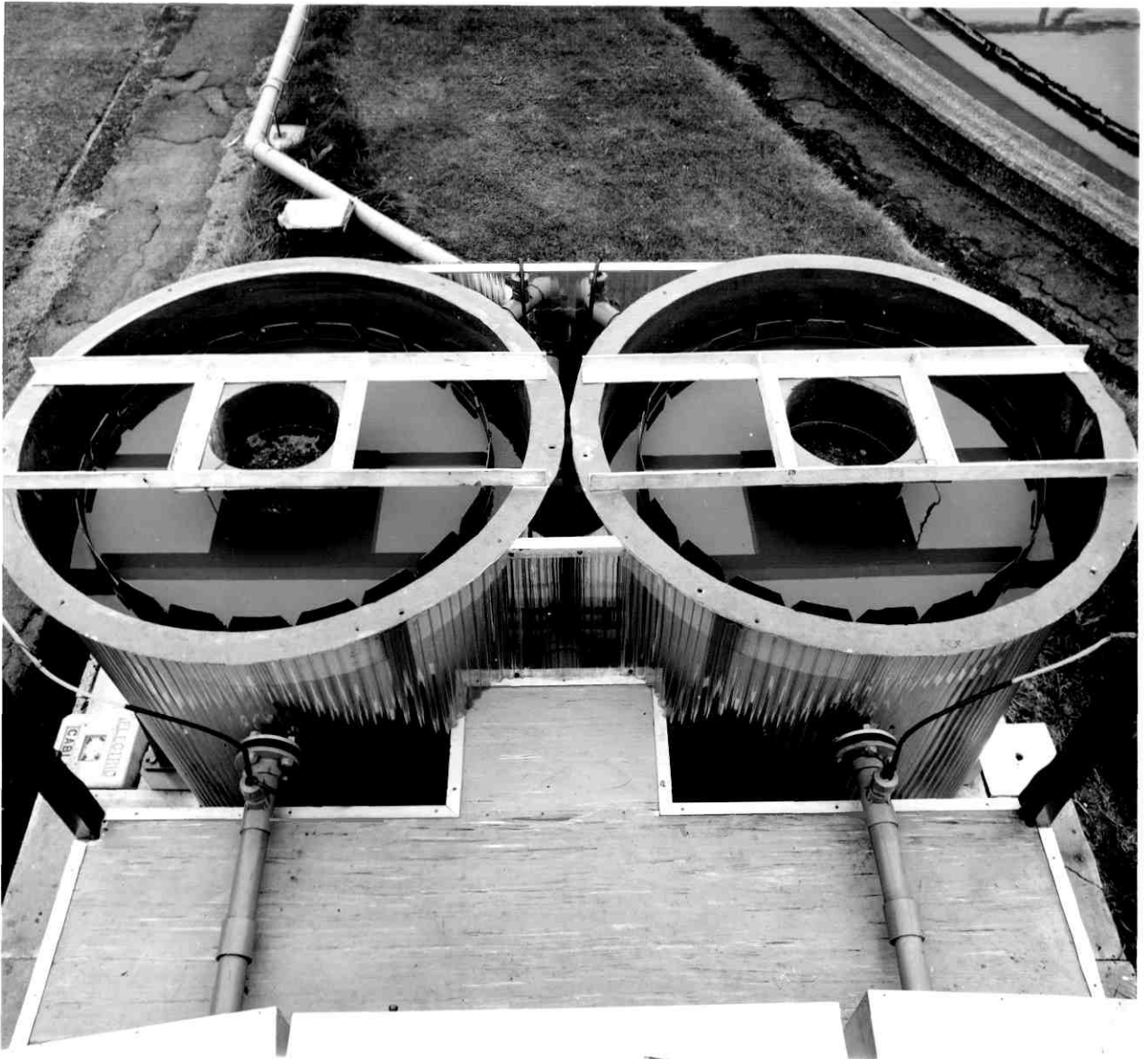


Plate 5 - Plan view of the Primary Sedimentation Pilot Plant tanks.



Plate 6 - Front view of the Primary Sedimentation Pilot Plant tanks.



Plate 7 - Rapid mixing and sampling systems of the Primary Sedimentation Pilot Plant.



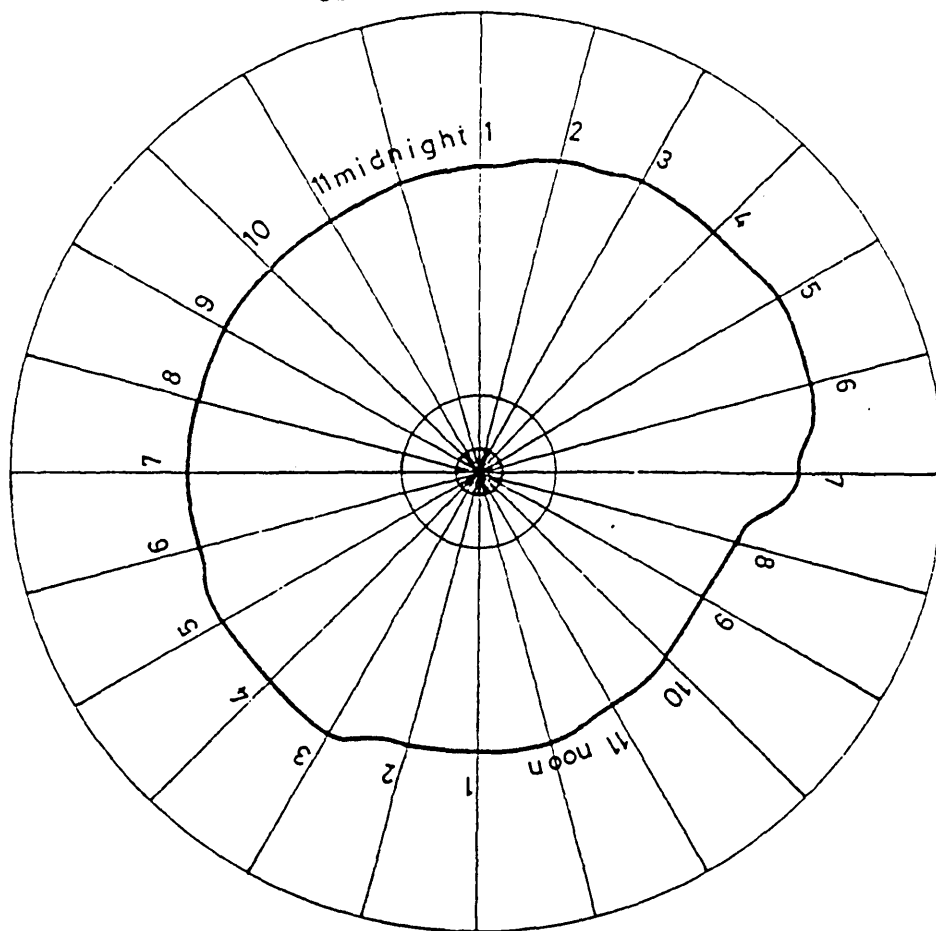
Plate 8 - Dosing system and electric control panel of the Primary Sedimentation Pilot Plant.

3.1.2.3 - Constant head loading and distribution systems

A picture of the whole system is shown in Plate 3. The sewage was delivered into a perspex tank with two main compartments. Perspex was chosen because it is transparent, easily machined and has a low metal content. The first compartment, where sewage was delivered, provided a constant level by diverting the excess flow over two lateral rectangular weirs. These weirs limited the variation in the level of the influent sewage to less than 9 mm at the maximum flow of 1.11ls^{-1} . The second compartment divided the sewage via two further adjustable rectangular weirs for delivery to both sedimentation tanks. These two compartments were separated by a perspex wall in which was mounted an adjustable 30° V-notch weir, which was used to regulate the flow rate from the first to the second compartment. This angle was chosen because it permitted sensitive control of the flow rate and was less readily blocked. This 30° V-notch weir was designed for a maximum flow of 1.11ls^{-1} and its movement was regulated by a cam in which had been milled a peripheral groove designed to simulate a typical daily flow variation under normal dry weather flow conditions which occurred at the Hogsmill Valley Works. This is presented in Fig. 2. The cam was operated by an electric motor with a magnetic brake, Parvalux SD-18-MBM (M.R. Suppliers Ltd., London, U.K.) controlled by sequential timers (section 3.1.2.11) with which it was possible by stop-start operation to rotate the cam at the appropriate rate. Plate 4 includes the arrangement for variable flow simulation. The level of the two weirs in the second compartment were adjustable such that the sewage could be divided equally or unequally into two chambers, each discharging the sewage via 50 mm bore pipes to the corresponding sedimentation tank. All the weirs were protected by baffles to avoid turbulence on the surface of the liquid.

3.1.2.4 - Rapid mixing system

Between the second compartment of the distribution system and each sedimentation tank was a rapid mixing system consisting of a 155 mm ABS pipe, 400 mm in length with four perspex baffles mounted at the internal periphery of the tube. Sewage was introduced at the



Scale 1:2

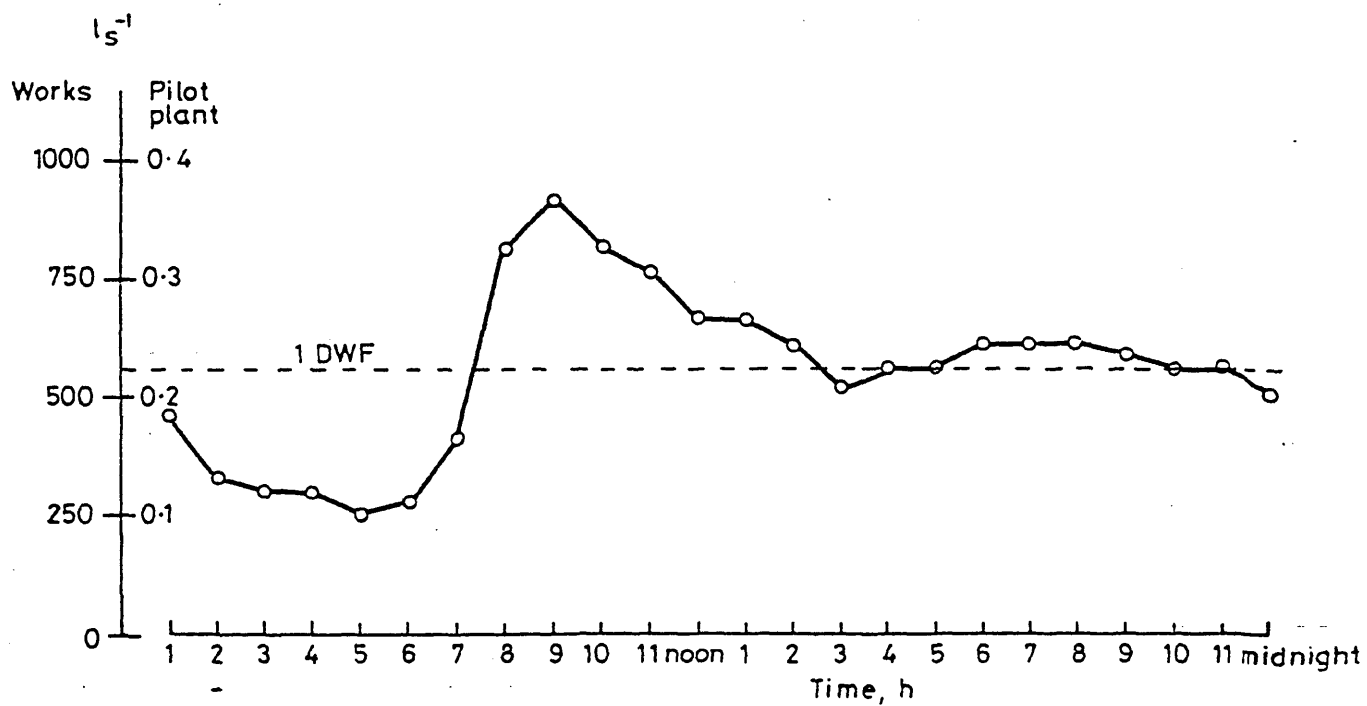


Figure 2 - Plan view of the flow control cam, and the typical daily flow variation under dry weather flow conditions at the Hogsmill Valley Sewage Treatment Works (Thames Water Authority, U.K.).

bottom and left from the top. Considering the inlet and outlet conditions it was decided to have a tank height to diameter ratio of 2.6:1 which is nearly double the value recommended by Rich (1961) for tanks having both inlet and outlet in the top. The influent sewage was mixed with "the detergent builder" rapidly by a stirrer (turbine type rotor) with eight stainless steel blades mounted on a stainless steel rod, driven by a Parvalux SD-11-MB electric motor (M.R. Suppliers Ltd., London, U.K.), running at $960 \text{ rev. min}^{-1}$. The tank diameter to impeller diameter ratio was 3 to 1 as suggested by Rich (1961). The retention times of the chamber were 62 and 21 s for flows of 0.111 and 0.333 l s^{-1} , respectively. With this system a Reynolds number of 35000 could be achieved assuming a liquid temperature of 21°C . The rapid mixing system is shown in Plate 7.

3.1.2.5 - Sedimentation tanks

The two identical tanks were operated in parallel. They were cylindrical at the top, with a diameter of 1 m and height of 1.10 m and conical (60°) at the bottom. The total height of the tank was 1.90m. The total capacity of the tank was 0.915 m^3 , with a retention time of 2.29 h at 0.111 l s^{-1} and 0.76 h at 0.333 l s^{-1} . The surface loadings were 0.56 and 1.68 m h^{-1} at 0.111 and 0.333 l s^{-1} , respectively. The sewage was introduced via a 50 mm ABS pipe into the centre of an internal drum of diameter 0.3 m and 0.8 m depth mounted centrally. The effluent passed over twenty one 45° V-notch weirs into a circular trough surrounding the top of the tank and was directed towards the outlet. Plate 5 is the plan view of the tanks.

Apart from the geometrical, mechanical and chemical similarities between both tanks, thermal similarity was obtained by mounting a screen around the tanks to avoid temperature variations due to wind. The sedimentation tanks were covered to prevent disturbance of the liquid surface. The sludge was discharged from the bottom of the tank through a 50 mm ABS pipe controlled by a diaphragm valve. A sampling valve was also provided to collect sludge samples from the tanks. Plate 6 includes the tanks, sludge discharge valves and sludge sample collection valves.

3.1.2.6 - Flow measurement

To permit measurement of the flow to both tanks, the effluents from them were collected alternatively into a measuring tank of 60 l

capacity and the time required to fill the tank determined. This operation was made possible by the use of a T-joint ball valve assembled in the effluent pipe. It was also possible to measure the total flow through both the pilot plants.

3.1.2.7 - Sludge discharge and measurement

The sludge was discharged via a 50 mm ABS pipe by a mutrator unit Model D 30 (Monopumps Ltd., London, U.K.) to a calibrated stainless steel sludge tank. The tank had a stirrer to permit mixing so that homogenous sludge samples could be collected.

3.1.2.8 - Detergent builder dosing system

The dosing system, shown in Plate 8, consisted of a calibrated 20ℓ aspirator made of borosilicate glass. The builder solution or suspension was stirred continuously with a glass rod to which were attached PTFE blades rotated by an electric motor. The solution or suspension (depending on which builder was being studied) was delivered by a peristaltic pump, multiperpex 2115 (LKB Ltd., Croydon, U.K.) via silicone rubber tubing to a point immediately prior to the rapid mixing tank of the test unit.

3.1.2.9 - Sampling system

Plate 7 shows the sampling system. Samples were collected from the raw and settled sewage by two Masterflex, variable speed, peristaltic pumps (Cole Parmer Instrument Co., Chicago, U.S.A.) with three heads on each. Samples were collected in borosilicate tall form beakers (150 mL) positioned in a static tray under a moving bridge mechanism to which were attached the flexible sample discharge pipes. The moving bridge was driven by a low speed electric motor with a magnetic brake (M.R. Suppliers, London, U.K.) via an endless rubber belt. For automatic sampling, both the movement of the bridge and the delivery of samples by the sampling pumps were controlled by sequential timers (Section 3.1.2.11).

The four sampling locations were:

Influent (control and test) - located in the feed pipe after the mixing chamber and before the sedimentation tank.

Effluent (control and test) - located in the effluent outlet pipe of each tank.

Effluent samples were collected using two heads of the sampling pumps connected to the sampling tube by a T-joint made of polypropylene, so that two samples of each effluent were collected since two preservatives were used. The volume of samples remaining in the tubes after each sampling was the same for all the sampling points. All sampling tubes were made of silicone rubber, 5.5mm internal diameter. The system was enclosed to avoid contamination. Between each group of experiments, all borosilicate beakers were leached with 2% (V/V) analar nitric acid for at least 24 h and rinsed with distilled water before use.

3.1.2.10 - Drainage and interconnecting pipework

The pilot plant was provided with a main drain which discharged into the primary sedimentation effluent collecting chamber of the Hogsmill Valley Works. All the wastage from the pilot plant was via this drain. The pipes which connected the constant head loading and distribution tank to the sedimentation tank and the sedimentation tank to the measuring tank were of 50 mm ABS. Escritt (1972) suggests values for velocity in pipes between 20 and 30 cm s^{-1} to avoid deposition of organic matter. To satisfy this condition the pipes should have had a diameter of not more than 25mm, however it was decided to use 50 mm ABS pipes because pipes of this diameter could be cleared easily where as a smaller diameter than 50 mm would have caused problems. Thus the velocity in these pipes was 5.7 cm s^{-1} and 17 cm s^{-1} for flows 0.111 ls^{-1} and 0.333 ls^{-1} , respectively, and some deposition was expected.

3.1.2.11 - Electrical and sequential timer control panels

Power for the pilot plants was supplied from the Hogsmill Treatment Works' main power supply through an electrical control panel located within the pilot plant building. The control panel incorporated an isolating switch for each electrically powered component. A switch for rapid cut-out of the whole pilot plant power supply was provided in case of emergency. Operations controlled by sequential timers relied on a long period timer initiating a short period timer which controlled the motors, a relay switch restarted the long period timer when the short period one had finished its cycle. The timers were Omron STP (Tateizi Electronics Co. Ltd., Japan).

3.1.3 Experimental Programme

The pilot plant was used to simulate the full scale plant under different hydraulic loading conditions. Twelve experiments were designed to study the effects due to zeolite type A or nitrilotriacetic acid on the effluent quality and plant performance and they were as follows:-

- Experiment I : 30 mg l^{-1} zeolite type A at 1 DWF.
- Experiment II : 30 mg l^{-1} zeolite type A at 3 DWF.
- Experiment III : 30 mg l^{-1} zeolite type A at variable flow condition.
- Experiment IV : 60 mg l^{-1} zeolite type A at 1 DWF.
- Experiment V : 60 mg l^{-1} zeolite type A at 3 DWF.
- Experiment VI : 60 mg l^{-1} zeolite type A at variable flow condition.
- Experiment VII : 15 mg l^{-1} NTA at 1 DWF
- Experiment VIII: 15 mg l^{-1} NTA at 3 DWF.
- Experiment IX : Variable concentration (6 - 34 mg l^{-1}) of NTA at variable flow condition.
- Experiment X : 30 mg l^{-1} NTA at 1 DWF.
- Experiment XI : 30 mg l^{-1} NTA at 3 DWF.
- Experiment XII : Variable concentration (10 - 66 mg l^{-1}) of NTA at variable flow condition.

Each group of experiments lasted for three days. Each experiment consisted of a series of stages. These are presented in Appendix I.

3.1.4 Operation and control

For each experiment the plants were operated continuously with the builder solution being dosed from the beginning. Normally the experiment started at 15:00 and the plants were left to stabilize during the night. At 12:00 on the third day, the whole system was stopped. Sludge was not removed from the plant during the experiment. At the end of the experiment 80ℓ of the supernatant from each tank was kept and the remaining liquid was discharged in the sludge tank using the system described in section 3.1.2.7. When all the liquid was discharged, the 80ℓ of supernatant was poured into the tanks to wash the discharge pipe and the pump and ensure that all the solids reached the measuring system. To guarantee both plants were operated under similar conditions in a stable manner, two measurements received special attention: flow rate (total and individual) and temperature (maximum and minimum). The first was determined as described in section 3.1.2.6, the temperature was measured using a maximum and minimum mercury thermometer, type Speed set (G.H. Zeal Ltd., London, U.K.) with 1°C divisions.

The performance of the pilot plants was comparable to the full scale Works as can be seen from the data in Appendix VIII.

3.1.5. Sampling procedure

The sampling programme was designed principally to obtain information about the effect of the builders on effluent quality and it was therefore decided to collect individual samples at 3h intervals starting at 9:00 h on the second day after the plant had stabilised. However, to calculate the mass balance during the experiment it was necessary to collect samples during the stabilisation period at the same interval. During experiments at constant flow a composite sample was generated by mixing 50 ml from each individual sample. During variable flow experiments no composite samples were generated.

3.1.5.1 Influent and effluent sampling

Six samples were collected at each sampling time as follows:

- 1 - Influent - for suspended solids and phosphate determinations.
- 2 - Influent - for metal determination
- 3 - Effluent control I - for suspended solids and phosphate determinations.
- 4 - Effluent control II - for metal determination.
- 5 - Effluent test I - for suspended solids and phosphate determinations.
- 6 - Effluent test II - for metal and builder determinations.

Influent and effluent grab samples were also collected for pH and ammonia determinations.

3.1.5.2 Sludge sampling

Sludge samples were collected manually from the sludge tank. These samples were collected in two batches because the sedimentation tanks were cleared in two stages, and a stainless steel stirrer was used to mix the contents of the sludge tank thoroughly for 3 min to get a representative sample. The sludge samples were collected for suspended solid, volatile suspended solids and metal determinations.

3.1.5.3 Sample preservation

For total inorganic phosphate determination, the samples were filtered through GF/C glass microfibre filter (Whatman Labsales, Maidstone, U.K.) and preserved with 2 ml of mercuric chloride solution (2 g l^{-1}) after collection. Mercuric chloride is an effective preservative in preventing hydrolysis of condensed phosphate in filtered waste water, for storage up to one week at room temperature (see section 4.1).

Samples for metal determination were collected in 150 ml borosilicate beakers containing 10 ml of 10% V/V analar nitric acid to reduce loss due to adsorption onto the walls of the glassware (Batley and Gardner, 1977) and transferred to 10ml borosilicate volumetric flasks. Samples for COD determination were preserved as described above. For NTA determination, the samples were preserved with 2 ml of mercuric chloride solution (2 g l^{-1}) to prevent biodegradation.

3.1.5.4 Sample pretreatment for metal analysis

Sludge samples were homogenized for 2 min using a modified T45N Ultra Turrax (Scientific Instrument Co., London, U.K.) the suitability of which has been described previously (Stoveland *et al.*, 1978) and then diluted 10 times with 1% (V/V) analar nitric acid and finally transferred to 10ml borosilicate volumetric flasks. For influent and effluent samples no pretreatment was required.

3.1.6 Zeolite dosage

The expected concentration of zeolite type A in sewage if polyphosphate is totally replaced by zeolite type A has been estimated by Hopping (1978) and Maki and Macek (1978) to be an average 10 mg l^{-1} of zeolite in the U.S.A., while in Germany, Fisher *et al.*, (1978) predicted values as high as $50 - 60 \text{ mg l}^{-1}$ in hard water areas. By calculation Stoveland *et al.*, (1979c) found that 1 mg l^{-1} STPP (as P) is equivalent to 9.81 mg l^{-1} of zeolite. Hence, if detergent builders contribute 5 to 10 mg l^{-1} of phosphate (as P) to the sewage, the theoretical zeolite concentration in sewage will be 50 to 100 mg l^{-1} .

Because of the inferior performance of zeolite type A, it is proposed that zeolite will only be used as a co-builder with STPP (Berth, 1978) so a value of 25 to 50 $\text{mg}\ell^{-1}$ of zeolite in sewage is a reasonable estimate. In this study therefore, zeolite type A was dosed at 30 $\text{mg}\ell^{-1}$ and 60 $\text{mg}\ell^{-1}$.

3.1.6.1 Preparation of Ca-exchanged zeolite type A

Before the zeolite reaches the sewage treatment plant, some ion exchange has already taken place, and the percentage exchange was assumed to be 25% which corresponds to the amount of exchange to be expected after a washing operation (Henning *et al.*, 1977). To simulate this, the zeolite suspension was mixed with calcium chloride before dosing. The exchange capacity for Ca is 0.14 gg^{-1} zeolite (Stoveland, 1978) assuming 100% exchange. So, for 25% exchange, 1 g zeolite requires 0.035 g Ca or 0.097 g CaCl_2 .

In this study, 22 ℓ of zeolite suspension was prepared, using glass distilled water, and the appropriate amount of calcium chloride was added and mixed thoroughly. The zeolite used in this study was produced by Henkel KGaA, Dusseldörf, Germany. Upon drying for 1 h at 105°C samples from the zeolite used in these experiments yielded an average reduction in weight of 9%.

3.1.7 NTA dosage

It has been calculated that if STPP were to be completely replaced by NTA, the concentration of NTA in domestic sewage would be between 10 and 20 $\text{mg}\ell^{-1}$ (Moore and Barth, 1976; Mottola, 1974). Higher concentrations in hard water areas, such as in Germany, have been suggested by Stoveland *et al.*, (1980b). So a value of 15 $\text{mg}\ell^{-1}$ and 30 $\text{mg}\ell^{-1}$ (as NTA^{3-}) was chosen for this study. A stock solution of 22 ℓ was prepared, using glass distilled water and the appropriate amount of NTA.Na_3 (Gold Label, trisodium salt of NTA, Aldrich Chemical Co., U.S.A.).

3.1.8 General maintenance

As raw sewage was to be treated in this pilot plant, special attention during the design stage was given to avoiding dead zones or sharp edges where coarse materials could accumulate and make

operation of the plant difficult. However, it was impossible to avoid completely this problem and thus a maintenance programme was required before, during and after each experiment. Special care was taken with the intake system and the drum was cleaned before the start of the experiment and during each of the additional two days of operation. To do this the system was stopped for 10 min and all the fibres and grease were removed and washed with pressurised water. At midday on the second day of the experiment when the temperature in the tanks was measured, the troughs surrounding the sedimentation tanks were cleaned. This was necessary because of the accumulation of small particles. Upon completing the experiment the plant was emptied and washed with tap water. The top of the settlers and the trough were brushed and washed. The rapid mixing system was disassembled, the blades cleaned of fibres and the system re-assembled. All the sampling points were inspected and cleaned. After initiating the experiment and before sampling the sampling pumps were switched on and all the sampling pipes were flushed with fresh sewage. Before the experiments at variable flow the rubber ring which prevented leakage through the movable weir was lubricated with silicone grease.

3.2 Activated Sludge Pilot Plant

3.2.1 Description

3.2.1.1 General description

The pilot scale diffused air activated sludge treatment plant was designed at the Imperial College (Carrondo, 1979) and assembled at the Thames Water Authority's Hogsmill Valley Sewage Treatment Works. It consists of two identical units working in parallel. The plants were supplied with settled sewage through a common supply system and the conditions in both were maintained as similar as possible so that experimental work could be undertaken using one of them as a control.

The building where the plants are housed is located near the primary sedimentation tanks and it includes a room used as a laboratory where most of the routine analyses were carried out. The plants were designed to operate under constant flow conditions (although between experiments flow could be varied). The laboratory section of the pilot plant building could be isolated from the pilot plants themselves by

a pair of heavy duty timber sliding doors. Within the pilot plant section, the room temperature was maintained at a predetermined value ($17^{\circ}\text{C} \pm 3^{\circ}\text{C}$) by a thermostatically controlled Qualitair cooling and heating unit (Chrysler Airtemp Ltd., Maidstone, U.K.) The flow diagram presented in Fig. 3 provides a diagrammatic representation of the plants and Plates 9, 10 and 11 show the various components.

3.2.1.2 Settled sewage supply system

The settled sewage supply system was common to both plants. A three head plunger metering pump type L (Metering Pumps Ltd., London, U.K.) drew the settled sewage from the outlet chamber of one of the primary sedimentation tanks at the Works and pumped it through a counter current coil type heat exchanger, Ref. HE 6/10, (Corning Ltd., Stoke-on-Trent, U.K.) to a 11 ℓ capacity reservoir. This reservoir contained a temperature probe connected to a thermocirculator (Churchill Instruments Ltd., Greenford, U.K.) which controlled the temperature of the liquid inside the heat exchanger coil. The reservoir contents were continuously mixed by a stirrer consisting of PTFE paddles mounted on a borosilicate glass shaft and driven by an electric motor, and a constant level was maintained by continuous discharge to waste of the excess inflow over a "V" notch weir. A peristaltic pump Type HBSV (Watson-Marlow Ltd., Falmouth, U.K.) equipped with a variable gearbox allowing for flows from 8 to 91 $\ell \text{ h}^{-1}$, pumped the sewage from the reservoir to both aerators through 10 mm diameter flexible silicone rubber tubes. Plate 9 is a view of the settled sewage supply system.

3.2.1.3 Aerators and compressed air system

The aerators were built of 300 mm nominal diameter QVF pipe (Corning Ltd., Stoke-on-Trent, U.K.) with an inverted vessel cover at the bottom connected by standard cast iron flanges with PTFE gaskets and had an effective volume of approximately 63 ℓ . Air to the aerators was supplied by a double head diaphragm pump, Duplex 4N, (Charles Austen Pumps, Ltd., Weybridge, U.K.) and delivered to the aeration units through 12 mm diameter PVC pipes. The air flow to both aerators was roughly controlled by adjusting a condenser tap. The fine setting of the air flow to each aerator being achieved by the adjustment of needle valves installed in the flow gauges (Gapmeter,

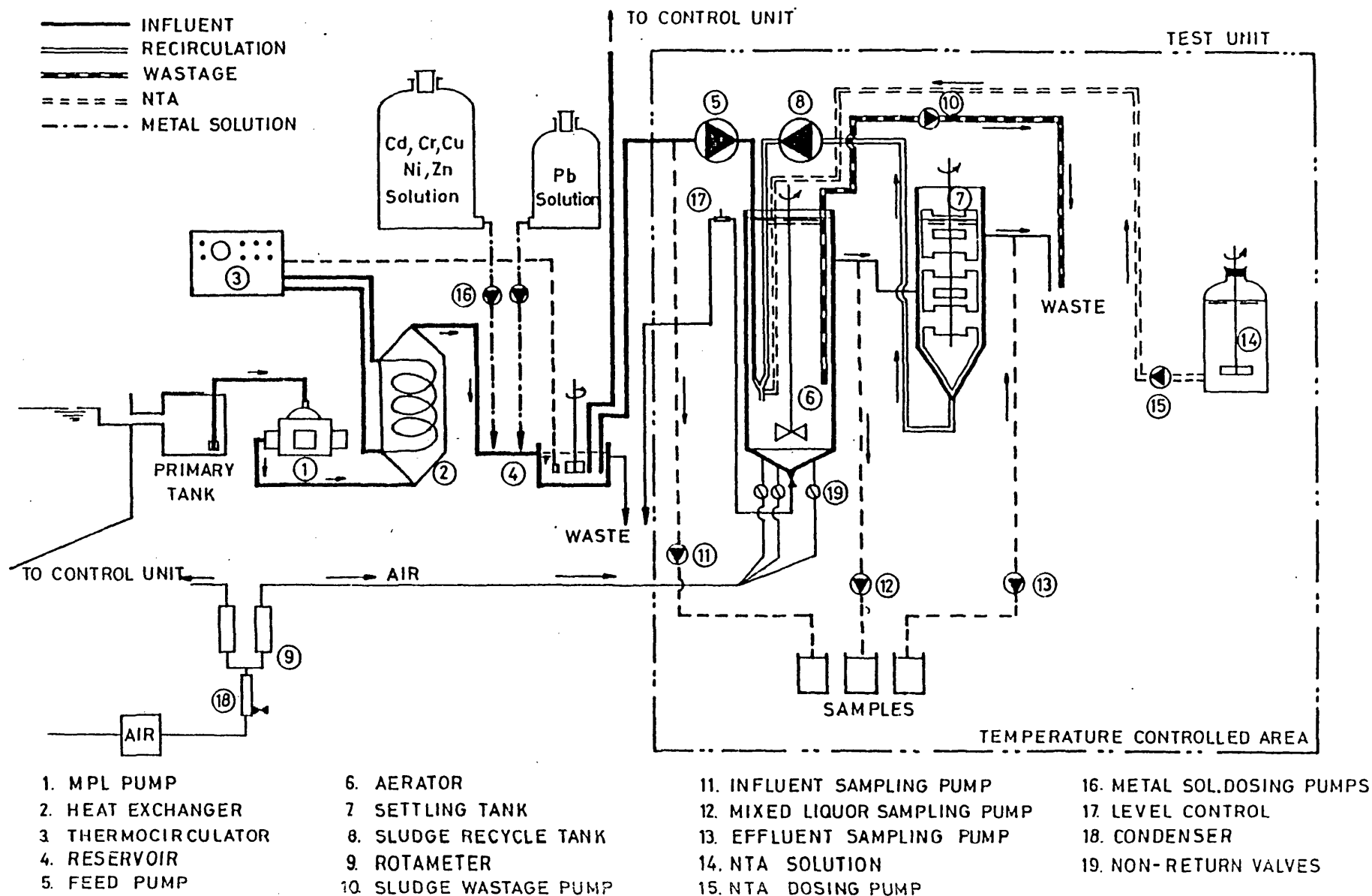


Figure 3- Diagram of the activated sludge pilot plant

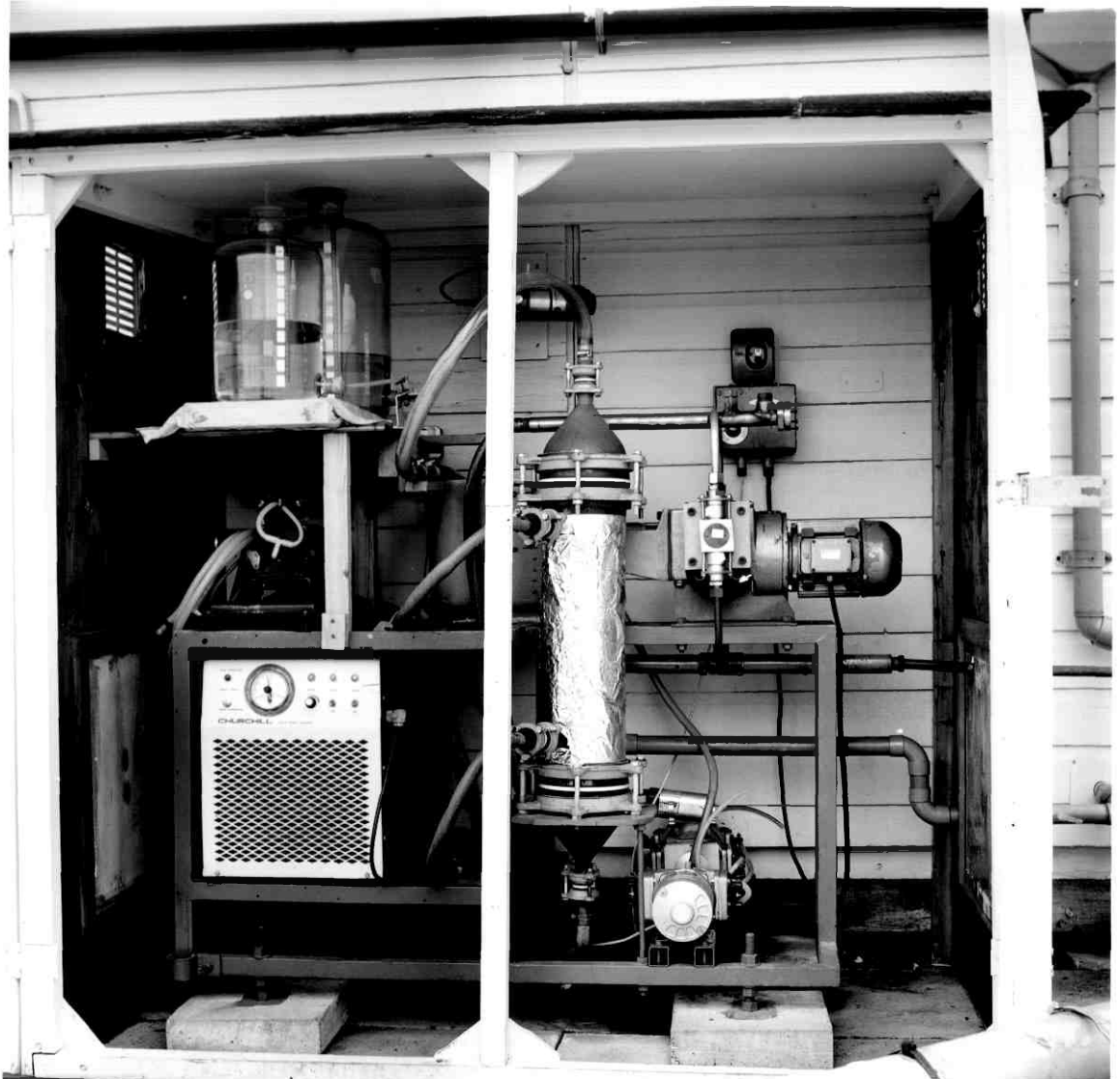


Plate 9 - Influent settled sewage supply and metal dosing system of
the Activated Sludge Pilot Plant.

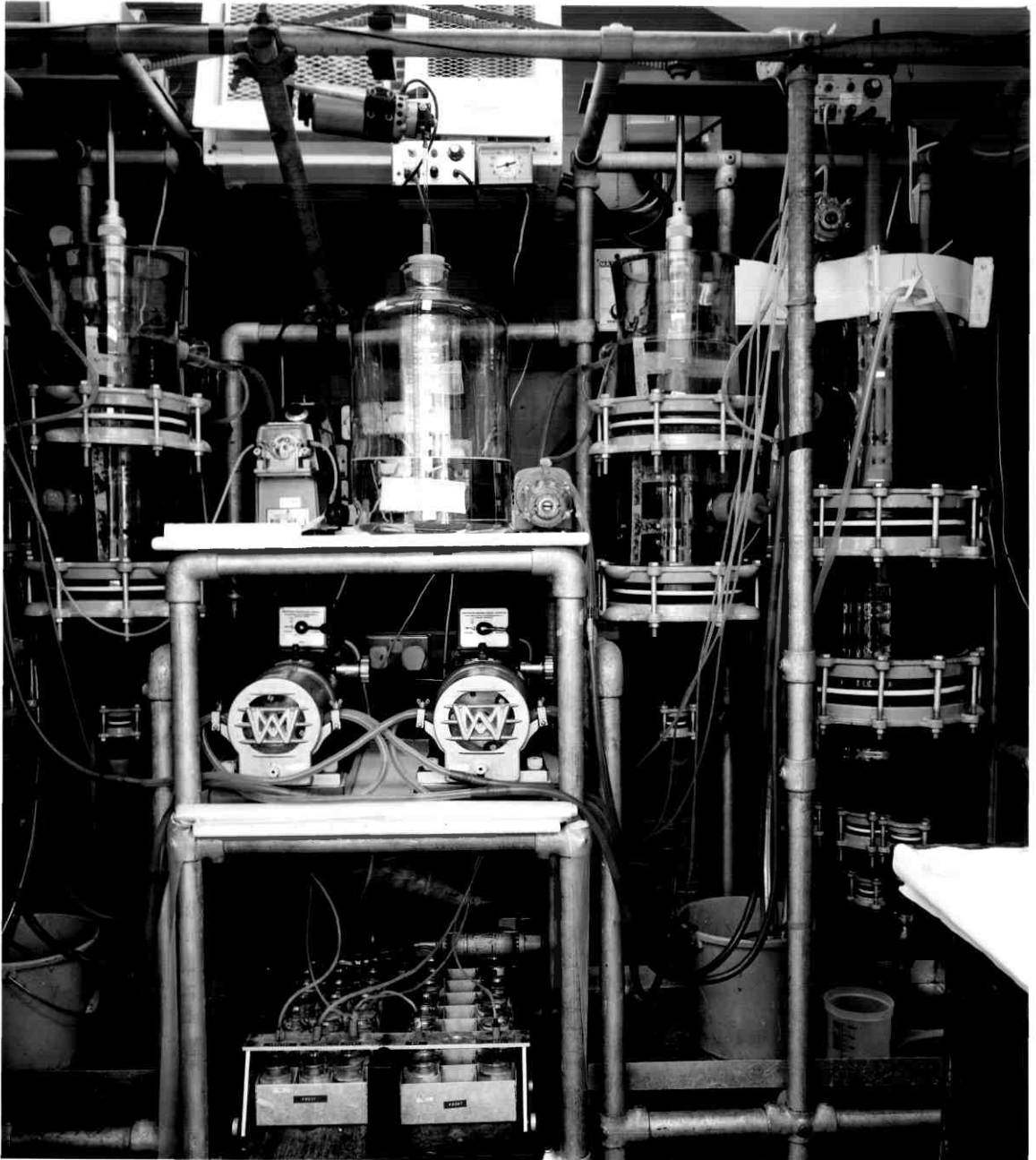


Plate 10 - General view of the Activated Sludge Pilot Plant.

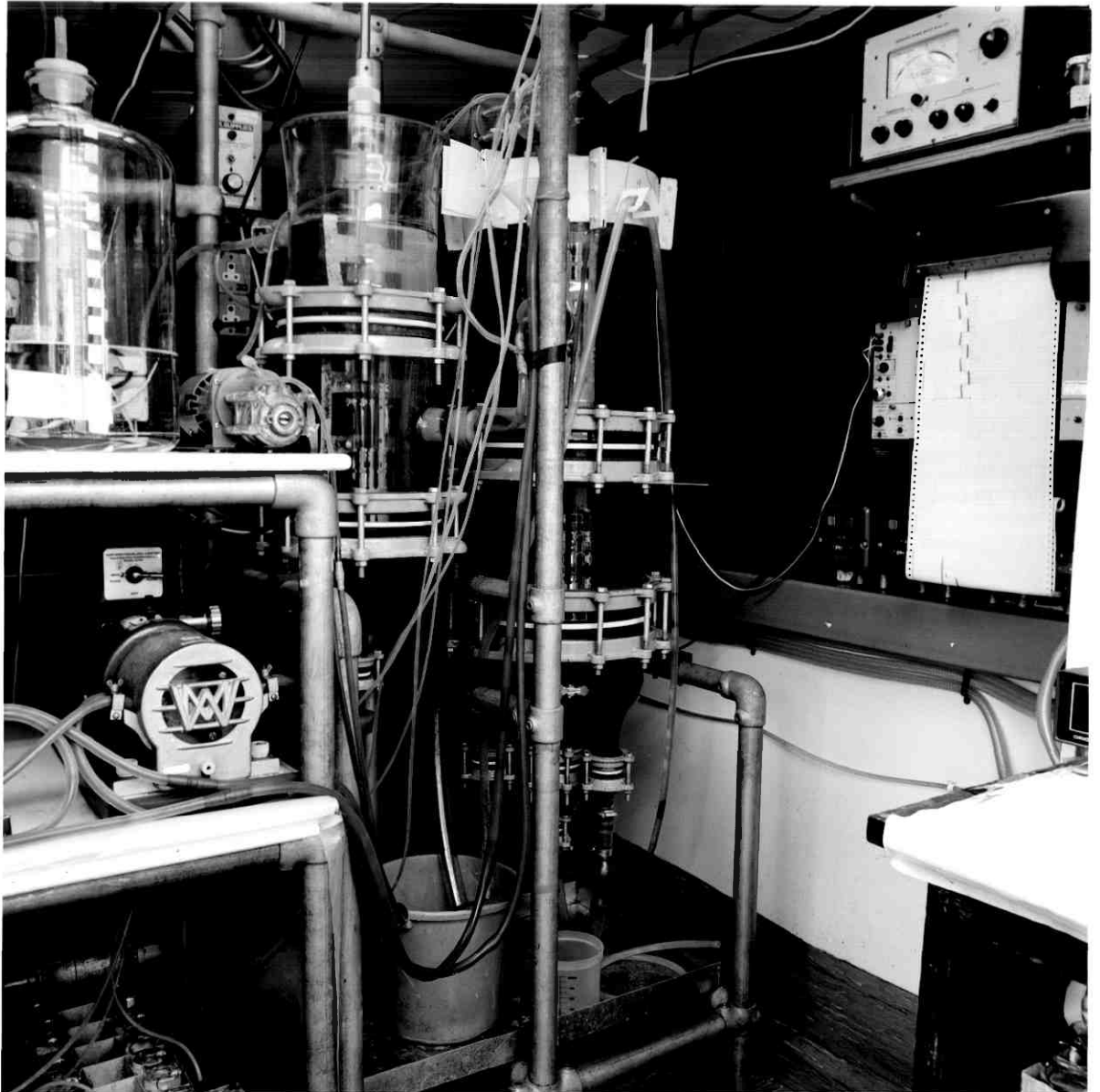


Plate 11 - Individual activated sludge pilot plant including dissolved oxygen meter and recorder.

Flowbits, Basingstoke, U.K.). In the bottom of each aeration tank were located three air diffusers made of sintered glass filters, porosity 2 (Gallenkamp, London, U.K.) placed in symmetrically spaced orifices, providing a fine bubble aeration system. Upstream of the diffusers in the air lines were Griffin bellows (Gallenkamp Ltd., London, U.K.) used as a non-return valve, to prevent the accumulation of liquid in the air system in the event of a breakdown in the air supply. An emergency air supply was also incorporated into the equipment via compressed air cylinders which were used in the event of a total power failure at the Works. Although stirring facilities were provided in both reactors they were never used because completely mixed conditions, on which the design was based, were achieved by the effect of aeration mixing alone. Connections between the aerators and the settling units were by silicone-rubber tubing inserted through orifices sealed against leakage by silicone rubber bungs bored to receive the connecting tubes with a leak-proof fit.

3.2.1.4 Settling units

The settling units were made of the same materials as the aerators and had a capacity of 20 ℓ and a nominal diameter of 225 mm. A PTFE paddle scraper fixed to a borosilicate glass shaft rotating at $0.25 \text{ rev min}^{-1}$ assisted sludge thickening and removal. The shafts were driven by a low speed motor (M.R. Suppliers, London, U.K.) providing direct power transmission to one of them and indirect transmission to the other by two endless rubber belts. The recycled sludge left via the bottom of the settler and the effluent was discharged to waste at the top through a 10 mm diameter pipe. Sealing against leakage was effected using silicone rubber bungs in the same manner as the aerators.

The settled sludge was collected from the base of the settling units and pumped to the respective aerator by a peristaltic pump similar to the one used for the settled sewage supply system. The pipes were identical to the ones used for the settled sewage supply system. Recycle of sludge to the aerators was made in conjunction with the influent settled sewage via a branched glass fitment that ensured mixing of the two before discharge.

3.2.1.5 Sludge wastage

Sludge wastage was made directly from the aerators using a variable speed peristaltic pump, Masterflex (Cole-Palmer Instruments Co., Chicago, USA) via 4 mm diameter silicone rubber tubing. The wasted mixed liquor was discharged to a 30 l plastic container. The frequency and duration of discharges was automatically controlled by sequential timers.

3.2.1.6 Sampling system

Sampling points were located as follows:-

Inlet - On the suction side of the settled sewage supply pipe to the control plant. Only one sampling point was provided for the two plants.

Mixed Liquor - in the connecting pipe between each aerator and the settling unit.

Effluent - in the effluent discharge pipe from each settling unit.

Three Masterflex pumps, similar to those previously described for sludge wastage were used for sampling, double-headed units being used for mixed liquor and effluent and a single-headed unit for the inlet. Each pump was fitted with a 2 mm internal diameter silicone rubber pipe with a 2 mm wall thickness, the remainder being of 6 mm diameter silicone rubber pipe. The delivery pipes were vented to the atmosphere to ensure complete discharge after each sampling cycle and thus eliminate any accumulation of solids in the tubing. The samples were collected in 150 ml borosilicate tall form beakers set in two aluminium trays at ground level, under a moving bridge mechanism to which were attached the five flexible sample discharge pipes. The moving bridge was driven as described in section 3.1.2.9.

3.2.1.7 Electrical and sequential timer control panel

This was as described in section 3.1.2.11.

3.2.1.8 Interconnecting pipework

All pipes in contact with sewage were made of flexible silicone rubber and joined with borosilicate glass tubing to avoid metal contamination. The joints were bound first with PTFE tape and finally with insulating tape to further reduce contamination. The only exceptions were the pipes discharging sewage and sludge to waste which were flexible transparent PVC tubing. An overflow was provided for each aerator. When a blockage occurred in the pipes between the aerator and the settler the overflow was directed into polythene containers beside each plant. Thus when the blockage had been repaired the solids could be returned to the aerator.

3.2.2 Experimental programme

The experimental programme was designed to investigate the effect of activated sludge treatment on NTA biodegradation and of NTA on heavy metal removal in an activated sludge process. It was achieved by a series of experiments in which the behaviour of NTA and metals in the system for different situations, obtained by the variation of three main parameters (sludge age, NTA influent concentration, and heavy metals influent concentration) were studied. During the experimental work there were three distinct phases in the pilot plants: stabilization, acclimatization and response to a shock load. These may be defined as follows:

Stabilization: after cleaning the plant and having seeded it with unacclimatized activated sludge from the Hogsmill Valley Sewage Works, the plant was operated for a few days at the desired sludge age prior to the addition of NTA. The purpose of this stabilization phase was to achieve comparable conditions in both plants before the experiment commenced. When transition from one experiment to the next was made without emptying the plant, this stabilization period was obviously not required.

Acclimatization: began in each experiment when NTA addition commenced to the test plant influent at a rate of 7.5 or 15 mgℓ⁻¹

and ended when negligible NTA was detected in the effluent.

Response to shock loading: this corresponded to the simulation of a "wash-day" situation and was achieved by an increasing of the influent NTA concentration from 7.5 to 15 $\text{mg}\ell^{-1}$ or 15 to 30 $\text{mg}\ell^{-1}$ after acclimatization had been achieved (i.e. when no NTA was detected in the effluent). This phase was over when NTA concentrations in the effluent fell to negligible values with a sustained influent concentration of 15 or 30 $\text{mg}\ell^{-1}$.

Eight experiments were undertaken, each one containing the three phases described previously:

- Experiment I : 4 days sludge age; low NTA influent concentration; low heavy metals influent concentration.
- Experiment II : 9 days sludge age; low NTA influent concentration; low heavy metals influent concentration.
- Experiment III : 12 days sludge age; low NTA influent concentration; low heavy metals influent concentration.
- Experiment IV : 9 days sludge age; low NTA influent concentration; high heavy metals influent concentration.
- Experiment V : 4 days sludge age; high NTA influent concentration; high heavy metals influent concentration.
- Experiment VI : 9 days sludge age; high NTA influent concentration; high heavy metals influent concentration.
- Experiment VII : 12 days sludge age; high NTA influent concentration; high heavy metals influent concentration.
- Experiment VIII : 9 days sludge age; high NTA influent concentration; low heavy metals influent concentration.

A further two experiments were undertaken to study the biodegradation of NTA at 4 d sludge age at both high and low heavy metals influent concentration.

- Experiment IX : 4 days sludge age; high NTA influent concentration; high heavy metals influent concentration.
- Experiment X : 4 days sludge age; high NTA influent concentration; low heavy metals influent concentration.

Details of the sequence and duration of each experiment are shown in Appendix II. The definition of low and high influent concentration of NTA and heavy metals are as follows:

Low NTA influent concentration - corresponded to an average of 7.5 mg l^{-1} (as NTA^{3-}). This is considered as being the lower limit for the normal range of NTA concentrations expected in settled sewage if NTA became the principal detergent builder. Most probably this concentration would be more representative of North American urban communities where water consumption 'per capita' is generally higher than in Europe (Stoveland et al., 1980b).

High NTA influent concentration - corresponded to an average influent concentration of 15 mg l^{-1} (as NTA^{3-}). This is considered to be the upper limit of the normal range of NTA concentrations to be expected in settled sewage. This figure represents the European situation (Stoveland et al., 1980b).

Low heavy metal influent concentration - corresponded to indigenous metals present in the influent settled sewage. As there is very little industrial area in the Hogsmill Valley Works catchment (Institution of Water Pollution Control, 1972) the situation simulates conditions for a non-industrialised urban community.

High heavy metal influent concentration - corresponded to the addition of heavy metals to the settled sewage to yield average influent concentrations typical of urban communities with developed and diversified industries (Stoveland et al., 1979a).

3.2.3 Operation and Control

3.2.3.1 Pilot plant operation

Throughout the experimental programme the pilot plants were operated at a constant nominal flow of 15 l h^{-1} which gave a nominal aeration time of 4 h. The mixed liquor was wasted at

different rates during the various experiments at sludge ages of 4, 9 and 12 d. The solids recirculation rate was generally maintained at a 1:1 ratio with respect to the flow of influent settled sewage, but for limited periods was increased to 1.5:1 in an effort to prevent the loss of solids during periods of sludge bulking. The "seed" mixed liquor for both plants was obtained from the return sludge channel of the Hogsmill Valley Works, which is not exposed to NTA. When the sludge age in the pilot plant was changed, the plants were emptied and washed before re-seeding with fresh return sludge, except during experiments II, V and VI, when organisms already acclimatized to NTA were utilised. All experiments were conducted at a temperature of $17^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in the mixed liquor. The mixed liquor temperature was controlled by varying the temperature of the influent settled sewage using the heat exchanger and by controlling the room temperature around the plants using the air conditioning system (as described section 3.2.1.1).

3.2.3.2 Plant control

To ensure that conditions in both control and test plants were similar as possible and to establish the similarity of the pilot plants and the full scale works which were comparable as can be seen in Appendix VIII, a number of operational parameters were monitored throughout the experiments in addition to those in section 3.8.1, these included room and mixed liquor temperature and the following:

3.2.3.2.1 Influent settled sewage loading and sludge recycle rate

The flow rate of both influent settled sewage and recycle sludge was checked daily by measuring its discharge for 2 min into a 1ℓ measuring cylinder. The maximum deviation allowed in both lines from the specified flow was $\pm 2\%$, the pumping rate was corrected whenever a larger deviation was observed. In both feeding and re-cycle pumps the pipes compressed inside the pumps were replaced every week.

3.2.3.2.2 Sludge wastage

The excess solids were removed from the system directly from the aeration units as described previously. The volume of mixed

liquor wasted every day from each reactor was 15, 6.67 and 5ℓ during experiments at 4, 9 and 12 d sludge age. The sludge wastage pumps were controlled by sequential timers which achieved most of the required wastage with discharges every 3 h during 12 d sludge age experiments and every 2 h during experiments at 4 and 9 d sludge age. Every day the volume wasted was measured and the volume taken for sampling added and the extra required to make up the desired volume was directly removed from the aerators. This procedure allowed for accurate control of the sludge age in both units.

3.2.3.2.3 Air supply

The control of the air flow was mainly dictated by the dissolved oxygen concentration in the mixed liquors, which was continuously monitored. The objectives for the air supply system were to ensure completely mixed conditions in the aerators and maintained the dissolved oxygen concentration between 0.5 and 1.0 mgℓ⁻¹. This range corresponds to the normal working conditions in full scale plants and was considered to be sufficient to achieve nitrification. However, it was impossible to predict the strength of the influent settled sewage and on some days low values for dissolved oxygen were observed and immediately corrected.

3.2.4 Addition of NTA

Solutions in distilled water of NTA (trisodium salt, monohydrate - $\text{N}(\text{CH}_2\text{CO}_2\text{Na})_3 \cdot \text{H}_2\text{O}$) manufactured by the Aldrich Chemical Company Inc., Milwaukee, U.S.A. were prepared as necessary, but at least once a week, in a 20 ℓ aspirator. A PTFE paddle stirrer system similar to that described previously for the feed reservoir ensured that the solution was uniformly and quickly mixed when each new batch was prepared. The NTA solution was dosed into the test plant through 1.6 mm diameter silicone rubber tube using a peristaltic pump, type MHRE/200 Mk3 (Watson-Marlow Ltd., Falmouth, U.K.) which was capable of delivery rates varying from 1.9 to 48 ml min⁻¹. The NTA dosage was checked daily by measuring the volume of solution delivered from the aspirator. An adjustment to the pump speed was made when necessary. This procedure allowed for the actual dosage to be very close to the nominal one. Very rarely did the error in the dosage rate exceed 10% of the nominal value.

3.2.5 Addition of heavy metals

Six of the so-called "heavy metals" were added to the settled sewage. The salts used to prepare the dosing solution and the intended influent concentration are given in Table 9.

Table 9 - Intended heavy metal influent concentrations and salts used to prepare dosing solution

Heavy Metal	Salt "Analar R" grade	Intended influent concentration mgℓ ⁻¹
cadmium	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.010
chromium	$\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.10
copper	Copper metal	0.10
lead	$\text{Pb}(\text{NO}_3)_2$	0.10
nickel	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.10
zinc	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.50

The metallic copper was dissolved in nitric acid prior to being added to the other salts in solution. All the metal salts, except lead, were dosed from a single 20 ℓ aspirator into the feed pipe to the settled sewage reservoir. The lead solution was made up separately to prevent precipitation of insoluble lead salts and added in a similar manner from a 10 ℓ aspirator. The dosage of the metal solutions was checked in a similar manner to the NTA solution.

3.2.6 Sampling procedures

A composite sample was prepared every day from the eight samples collected automatically from each one of the five sampling points, for COD and metal analysis. These samples were collected every 3 h in 150 ml borosilicate beakers containing 10 ml of 10% (V/V) analar nitric acid. Each morning the samples from each line were mixed up in 500 ml borosilicate glass flasks from which composite samples were taken. For metal analysis, influent and effluent samples were transferred to 10ml borosilicate volumetric flasks, while for mixed liquor the samples were first homogenized for 2 min with a modified model T 45 N Ultra Turrax, the same as referred to in Section 3.1.5.4., and then diluted 10 times.

with distilled water in 100 mL borosilicate volumetric flasks, from which samples were finally taken into 10 mL borosilicate flasks. The purpose of this dilution was to keep the metal concentration in all samples within the same range. Samples for COD analysis were also taken from influent and effluent composite samples and stored in 150 mL beakers for analysis every three days. Samples for phosphate analysis were filtered through a GF/C glass microfibre filter (Whatman Labsales, Maidstone, U.K.) and preserved using mercuric chloride solution to produce a concentration of 40 mg l^{-1} in the sample (see section 4.1). The samples were collected at approximately 17.00 h because that was thought to be the time of the daily peak concentration for phosphates in the sewage arriving to the Hogsmill Valley Works.

All the glassware used for metal and COD samples collection was leached with 2% (V/V) analar nitric acid for at least 12 h and the glassware for phosphate sampling was leached with 5% (V/V) analar sulphuric acid when not in use. For all other analytical purposes grab samples were taken from the relevant points in the plant using clean glassware and ensuring that the samples were representative. The samples taken for determination of sludge indexes were returned to the respective reactors after the test because of the significant amount of solids contained in them.

3.2.7 Biological Monitoring of the Mixed Liquor

Periodically throughout the experimental programme, samples of mixed liquor were taken from each plant and examined under a compound microscope at 1:100 and 1:400 magnification to compare the populations of protozoa, metazoa and filamentous bacteria. No attempt was made to compare the populations on a quantitative basis, but the continued presence or absence of particular species were noted.

3.2.8 General Maintenance

Complementing the normal procedures required for the operation of an activated sludge plant and due to the inherent modelling problems, special attention was paid to some peculiar features of the pilot plant. To avoid the growth of micro-organisms inside the inlet tubing a cleaning operation was performed every week by squeezing these pipes and wasting these materials. Two litres of mixed liquor were transferred every day from bottom to top in each aerator to make sure that anaerobic conditions did not develop in the dead zone below the diffusers.

The material accumulated on the internal free board of the aerators, due to splashing of mixed liquor, was removed daily into the liquid phase. The solids which were stuck on the walls and scrapers in the settling tanks were removed daily into the liquid to avoid possible development of anaerobic conditions and avoid deterioration of effluent quality.

3.3 Procedure for Activated Sludge Solids Adsorption Experiments

A volume of mixed liquor (625 ml) was taken and mixed with 176 ml of NTA stock solution (100 mg l^{-1} of NTA.Na_3) in a 1000 ml borosilicate beaker to give a concentration of 15 mg l^{-1} of NTA. The mixture was stirred continuously using a magnetic stirrer. 50 ml samples were taken after 1 min 15 s, 4 min 15 s, 7 min 15 s, 10 min 15 s and 19 min 15 s and filtered through a GF/C glass microfibre filter (Whatman Labsales, Maidstone, U.K.). The first 20 ml was filtered after 15 s and wasted, the remainder was filtered after 30 s, thus the average contact time for each sample with NTA before separation by filtration was 2, 5, 8, 11 and 20 min. The velocity of filtration was controlled by increasing or reducing the vacuum below the filter. The remaining filtrate was analysed for NTA (see section 3.8.1.11). Suspended solids analysis (section 3.8.1.1) was carried out using the residual mixed liquor in the beaker. Temperature was measured at the start and the end of the experiment. If the mixed liquor was spiked with metal the metal solution described in section 3.2.5 was used and mixed before adding NTA.

3.4 Alkalinity Tests

Alkalinity tests were carried out on sewage samples by adding NTA to the samples to achieve concentrations of 0, 7.5, 15 and 37.5 mg l^{-1} . Samples of settled sewage (100 ml) were used and dosed with a 10 g l^{-1} solution NTA.Na_3 to achieve the desired concentrations.

3.5 Determination of metal solubility

Grab samples of influent and effluent were collected twice daily from the control unit of the activated sludge pilot plant during experiments conducted at sludge ages of 4, 9 and 12 days. Samples were

split into two groups to determine "total" and "soluble" metal concentration. For total metal determination samples were transferred to 10 mL borosilicate volumetric flasks and preserved with 1% (V/V) analar nitric acid. "Soluble" and "particulate" forms of heavy metals were separated by membrane filtration using 'Nuflow' cellulose acetate fibres (Oxoid Ltd., Basingstoke, U.K.) with a pore size of 0.22 μm . This pore size represents only an arbitrary division between soluble and insoluble species of heavy metals. Although some workers have used 0.45 μm pore size filters, which have been adopted as a convention for separating insoluble species (Batley and Gardner, 1977), 0.22 μm filters have been used to ensure complete exclusion of bacterial cells from sample filtrates (Hayes and Theis, 1978). Before use, the filters were leached in 1% (V/V) analar nitric acid for 4h and rinsed three times in distilled water. An all pyrex filter holder (Gallenkamp Ltd., London, U.K.) was used for filtration. Prior to collection of the sample filtrate (up to 20 mL), distilled water (2 x 20 mL) and sample (20 mL) were passed through the filters. Filtrates were transferred to 10 mL borosilicate volumetric flasks and preserved with 1% (V/V) analar nitric acid. Metal analyses were carried out as described in section 3.8.2.

3.6 Chloride Tracer Tests

To assess the hydraulic characteristics of the primary sedimentation pilot plant and activated sludge pilot plant, chloride tracer tests were conducted. Background tests to compare test and control plant chloride ion concentration under normal conditions were also conducted.

3.6.1 Chloride tracer test for primary sedimentation pilot plant

Spike doses of 140 g sodium chloride diluted in 1 L distilled water were introduced to the test and control plants inlets just after the distribution weir. Samples were taken using the sampling system operated manually for influent and effluents. At the same time effluent samples were collected manually immediately after the T-joint valve in the measuring system to assess the effect of the liquid retained in the sampling pipe on the sample quality. The amount of sodium chloride was tripled for the test at 3 DWF condition.

3.6.2 Chloride tracer test for activated sludge pilot plant

Two separated tests were conducted in which spike doses of 5g sodium chloride were introduced to the test and control plants inlets and a continuous dose of 100 mg l^{-1} of chloride ion to the test plant inlet only. Chloride ion concentrations were monitored in the mixed liquor and effluent using the sampling system operated manually. Sludge wastage was stopped for the duration of the tests. For the continuous dosing of chloride to the test plant, a solution of sodium chloride in distilled water was prepared in a 3 l brown bottle and the same system of delivery as for NTA dosing was adopted.

3.7 Jar Test to Investigate the Effect of NTA on Metal Solubilization in Raw Sewage and Mixed Primary Sludge Samples, in the Presence or Absence of a Spiked Heavy Metal.

Two jar tests were performed using raw sewage and mixed primary sludge collected from the Hogsmill Valley Works which contains low concentrations of heavy metals (Nicholls *et al.*, 1980). To investigate the effect of NTA on metal mobilization in raw sewage and raw sludge under low and high metal concentrations part of the samples were spiked with metal solutions. The heavy metal solution added was calculated to yield concentrations normally found in industrialized areas as reported by Perry *et al.*, (1975), Lester *et al.*, (1977) and Stoveland *et al.*, (1979e).

3.7.1 Preparation of metal solutions

For the raw sewage experiment the samples were spiked with the solution containing Cd, Cr, Cu, Ni, Zn and a Pb solution containing 75 mg l^{-1} Pb. The lead solution was prepared separately so as to prevent the precipitation of lead sulphate since a sulphate salt of chromium was used. The five metal solution contained 1.07 mg l^{-1} Cd, 286 mg l^{-1} Cu, 5.8 mg l^{-1} Cr, 19.6 mg l^{-1} Ni and 500 mg l^{-1} Zn.

For the mixed primary sludge experiment the same procedure was adopted with a lead solution of 1250 mg l^{-1} as Pb and 5-metal solution containing 6.3 mg l^{-1} Cd, 153 mg l^{-1} Cu, 13 mg l^{-1} Cr, 14.5 mg l^{-1} Ni and 474 mg l^{-1} Zn. The metal salts used were as described in section 3.2.5.

3.7.2 Jar test on raw sewage

This experiment was designed to study the metal mobilization due to NTA under two conditions:-

- raw sewage - at indigenous low metal concentration.
- raw sewage - at high metal concentration, by adding metal.

An NTA solution of 750 mg l^{-1} was prepared, and added to the sewage sample such that it contained NTA at a concentration of 15 mg l^{-1} (as NTA^{3-}).

Four sample solutions were prepared in glass-stoppered borosilicate flasks, as shown in Table 10.

Table 10 - Preparation of raw sewage sample solutions

Volume in ml sample and reagent	Flask A (at low metal conc.) CONTROL (no NTA)	Flask B (at high metal conc.) TEST (15 mg l^{-1} NTA)	Flask C (at high metal conc.) CONTROL (no NTA)	Flask D (at high metal conc.) TEST (15 mg l^{-1} NTA)
raw sewage	240	240	240	240
distilled water	10	5	6.2	1.2
5-metal solution	-	-	2.8	2.8
Pb solution	-	-	1.0	1.0
NTA solution	-	5	-	5
total volume	250	250	250	250

These four sample solutions were put into a temperature controlled Tecam shaking bath SB-4 (Techne Ltd., Cambridge, U.K.) at the same time, and they were shaken at a speed of around 128 oscillations per minute, with a maximum lateral displacement of 20 mm (i.e. 10 mm to either side). The temperature of the water bath was maintained at $22^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.

Samples were collected for metal analysis. The sampling scheme was as follows:-

- an initial sample was collected before adding metals, to check if there was any difference between the raw sewage samples in the four flasks.

- b) a second set of samples was collected after 30 min of shaking
- c) further samples were collected every 0.5 h or 1 h, and the last set of samples was collected after 4 h shaking.

At every sampling occasion approximately 20 ml of sample was collected from each flask.

3.7.3. Jar test on mixed primary sludge

This experiment was designed to study the metal mobilization due to NTA under two conditions:-

- a) mixed primary sludge - at indigenous low metal concentration
- b) mixed primary sludge - at high metal concentration, by adding metal.

An NTA solution of 750 mg l^{-1} was prepared, and added to the sludge sample such that it would contain NTA at a concentration of 15 mg l^{-1} (as NTA^{3-}). Four sample solutions were prepared in glass-stoppered borosilicate flasks, as shown in Table 11.

Table 11 - Preparation of mixed primary sludge sample solutions

Volume in sample and reagent ml	Flask A (at low metal conc.) CONTROL (No NTA)	Flask B (at high metal conc.) TEST (15 mg l^{-1} NTA)	Flask C (at high metal conc.) CONTROL (No NTA)	Flask D (at high metal conc.) TEST (15 mg l^{-1} NTA)
raw sludge	220	220	220	220
distilled water	30	25	7	2
5-metal solution	-	-	19	19
Pb-solution	-	-	4	4
NTA solution	-	5	-	5
Total volume	250	250	250	250

The mixed primary sludge was homogenized with Ultra Turrax (as in section 3.2.6) so that homogenous samples were obtained for A, B, C and D. The same conditions for incubation were used as for previous raw sewage samples. The same procedure for collection of samples was adopted as before except that the last samples were collected 3 h after addition of NTA.

3.7.4 Ultracentrifugation

To study the metal mobilization due to NTA, an ultracentrifugation technique was employed to separate the soluble fraction of the sample from the insoluble fraction. The supernatant was then withdrawn carefully and collected for metal analysis. The samples were put into 8 ml thick wall polycarbonate centrifuge tubes, previously leached in 10% (V/V) analar nitric acid, with push on caps. Before they were loaded into the rotor, the oppositely positioned tubes were balanced to within 0.1g. The samples were centrifuged, using MSE Hi-Spin 21 Centrifuge with angle rotor 43114-142 (MSE, Scientific Instruments, Surrey, U.K.). Raw sewage samples were centrifuged at 21,000 xg for 10 min and mixed primary sludge at 10,000 xg for the same time.

3.7.5 Heavy metal determinations

The metal concentration of the supernatants were determined as described in section 3.8.2. For total metal concentration of the samples, only the initial and the last group of samples were analysed, to check if the control and the test were similar in their total metal contents, and to estimate the percentage distribution of heavy metals.

3.8 Analytical Methods

3.8.1 Routine analysis

3.8.1.1 Suspended solids and volatile suspended solids

These determinations were carried out according to the standard filtration procedure (Government of Great Britain, 1972). For influent and effluent in the primary sedimentation simulation 50 ml of samples were used and 10 or 25 ml for sludge samples. During the activated sludge studies 20 ml were used for mixed liquor samples and 200 ml for final effluent samples.

3.8.1.2 Sludge volume index

The sludge volume index was determined by the Standard Method (Government of Great Britain, 1972).

3.8.1.3 Dissolved oxygen

Dissolved oxygen concentrations in mixed liquors were determined using two dissolved oxygen probes immersed in the reactors and connected to a portable dissolved oxygen meter model 15A (Electronics Instruments Ltd., Surrey, U.K.). The measurements were continuously recorded on an Oxford 3000 Series potentiometric laboratory chart recorder (Oxford Instrument Co. Ltd., Oxford, U.K.).

3.8.1.4 Chemical oxygen demand

A modification of the Standard Method (Government of Great Britain, 1972) described by Matthews (1977) was used. Nine samples and two blanks were undertaken simultaneously (see Appendix III).

3.8.1.5 pH

An Orion 701 digital potentiometer with a pH electrode (Orion Research Inc., Cambridge, U.S.A.) was used for pH determinations. Influent and effluents from the primary sedimentation pilot plant and activated sludge pilot plant were analysed. Before each set of determinations the instrument was standardized against a buffer solution (pH 7).

3.8.1.6 Alkalinity

Alkalinity was determined by the Standard Method (Government of Great Britain, 1972) using the electrometric titration procedure in the same manner as for the pH determination described previously.

3.8.1.7 Hardness

Total hardness was determined by the Standard Method (Government of Great Britain, 1972).

3.8.1.8 Chlorides

Chloride concentration was determined by the Standard Method (Government of Great Britain, 1972) using the silver nitrate titration procedure.

3.8.1.9 Ammonia

Ammonia concentrations were determined using a potentiometer (see section 3.8.1.5) fitted with an ammonia specific ion electrode, model 95-10 (Orion Research Inc., Cambridge, U.S.A.).

3.8.1.10 Phosphates

Orthophosphate and total inorganic phosphates were determined in filtered and preserved samples by the recommended colormetric method (Government of Great Britain, 1972). The absorbances were recorded with a Pye-Unicam Sp-8-100 UV Spectrophotometer using 10mm glass cells. 1ml samples were used for orthophosphate determinations and 5ml samples for total inorganic phosphate determinations.

3.8.1.11 NTA Determination

The concentration of NTA was measured using the method developed by Longman, et al., (1971), but with certain minor modifications. The absorbance was determined using two different absorptiometers (Evans Electroselenium Ltd., Essex, U.K.) one with a No. 609 red filter and the other at a wavelength of 620 nm.

The cell size of the former required a sample volume of double the size recommended for the method used. The elutriation rate was never greater than the 1ml min^{-1} recommended and was usually in the range $0.5 - 0.75\text{ ml min}^{-1}$. Calibration standard solutions of 0, 2.5, 5, 10 and 15 mg l^{-1} NTA as the trisodium salt monohydrate were prepared. The zinc-zincon reagent was renewed at least every two weeks and a new calibration graph was prepared for each new batch of reagent, and before any test requiring numerous determinations.

The following procedure was adopted for the determination of the NTA concentration using the absorptiometer which required double volumes (figures in brackets indicate the volumes used when using the second absorptiometer):

Add 50 ml (25 ml) of reagent to 30 ml (15 ml) of each of the calibration solutions and measure the absorbance of each against distilled water to give the calibration absorbance.

Draw the calibration graph by plotting, on a linear scale, the solution's NTA concentration against its 'relative absorbance' ('relative absorbance' = 'Calibration absorbance' of blank - 'calibration absorbance' of solution).

For each elutriated sample for analysis, add 50 mL (25 mL) of reagent to 30 mL (15 mL) of sample and measure the absorbance against distilled water to give the 'sample absorbance'.

For each elutriated sample for analysis, add 50 mL (25 mL) of distilled water to 30 mL (15 mL) of sample and measure the absorbance against distilled water to give the 'sample blank absorbance'.

Calculate the 'sample relative absorbance' from ('calibration absorbance' of blank - 'sample absorbance' + 'sample blank absorbance') and determine the concentration of NTA in the sample from the calibration graph.

The NTA concentration in the dose solution was checked periodically by diluting a sample of the solution to within the range 0 to 15 mgL^{-1} and measuring the absorbance without elutriation. Six ion exchange resin columns were used and the resin was regenerated by the method recommended by Longman *et al.*, (1971), at least every four weeks and always before any test requiring numerous determinations. The columns were used in strict rotation to ensure that the resin in each column was used an equal number of times between the regenerations. The concentrations of NTA were expressed as the concentration of the ionic form of NTA, i.e. NTA^{3-} . However the concentration of NTA on the calibration graph was expressed as the trisodium salt monohydrate concentration, the ionic concentration being obtained by dividing by 1.4625.

3.8.1.12 Zeolite determination

Zeolite concentration can be determined by analysis of the aluminium content of the sample, if the background aluminium concentration is known. Flameless carbon furnace atomic absorption spectrometry was employed for the determination of the aluminium content, and complete

recovery in waste waters has been shown with various additions of zeolite solution (Carrondo et al., 1979a). Control and test samples were analysed, and the background aluminium concentration was estimated from the results obtained from the control samples. By subtraction the zeolite concentration in the test samples were determined, knowing that the percentage of aluminium in zeolite type A is 15.08. Conditions for flameless atomic absorption are described in section 3.8.2.2.

3.8.2 Metal analysis

3.8.2.1 Instrumentation

Analysis of aluminium, cadmium, chromium, copper, lead, nickel and zinc were carried out using Perkin-Elmer models 305, 603 and 5000 atomic absorption spectrophotometers (Perkin-Elmer Ltd., Beaconsfield, U.K.) fitted respectively with heated graphite atomisers HGA 72, HGA 76 and HGA 500. The instruments were equipped with deuterium background correction although it was only used for cadmium, lead and zinc analysis. Single filament hollow cathode lamps have been used for all analyses.

3.8.2.2 Analytical methods

The flameless atomic absorption analysis for metal determination in sewage and sewage sludge samples were reported by Carrondo et al., (1979b) and Stoveland et al., (1979d).

The analytical conditions used are included in Table 12 and the electrothermal atomization programmes in Table 13.

Samples were injected with 20 or 50 μl Eppendorf micropipettes (Anderman and Co. Ltd., Surrey, U.K.) using plastic disposable tips. The tips were rinsed with 10% (V/V) analar nitric acid and distilled water and sample before injection to reduce contamination between injections. Frequent replacement of the tips was inevitable because the high content of organics in the samples which caused the loss of the non-wettable nature of the tips.

Duplicate measurements were taken for composite samples, mixed liquor samples and sludge samples while for individual samples, the analysis was performed in a pairwise fashion, to reduce error due to baseline drift and change in calibration, (i.e. influent 1, effluent control 1, effluent test 1, influent 2, effluent control 2,). Standards were checked every 10 to 15 injections, to see if there was any change in the calibration.

Table 12 - Analytical conditions for electrothermal atomic-absorption analysis

Metal	wavelength, nm	spectral width, nm	working range mg l^{-1}	sample volume, μl	background correction
Al	257.5	0.2	0.2-5.0	20	without
Cd	228.8	0.7	0.005-0.03	20	with
			0.002-0.02	50	with
Cr	358.0	0.2	0.02-0.2	20	without
			0.005-0.05	50	without
Cu	324.7	0.7	0.05-0.5	20	without
			0.02-0.2	50	without
Pb	283.3	0.7	0.025-0.4	20	with
			0.010-0.2	50	with
Ni	232.0	0.7	0.10-1.0	20	without
			0.05-0.4	50	without
Zn	307.6	0.7	0.2-2.0	20	without
			0.05-1.0	50	with

3.8.2.3 Standards

Working standards were prepared freshly every week from stock solutions containing 1000 mg l^{-1} of the metal concerned. All standards were prepared with glass distilled water and contained 1% (V/V) analar nitric acid.

3.8.2.4 Glassware

Borosilicate glassware was used throughout. It was previously cleaned with tap water and leached with 1% (V/V) analar nitric acid. After three rinses with distilled water, they were ready for use.

3.9 Estimation of Metal Mobilization from the Fibre Glass Sedimentation Tanks

An experiment was performed to investigate the effect of NTA on mobilization of metals from the fibre glass employed to build the sedimentation tanks. A square piece of fibre glass, identical to that used to build the tanks, measuring $5 \times 5 \text{ cm}$, was fixed vertically into a beaker, 371 ml of settled sewage was poured into the beaker covering all of the specimen and stirred using a magnetic stirrer. NTA Na_3 was added to produce a concentration of 30 mg l^{-1} as NTA. Samples were taken 1 min

Table 13 - Electrothermal atomiser programmes for flameless atomic absorption analysis

Metal	Temperature Time	Drying	Ashing		Atomization	Gas flow
Al	°C	100	450	1200	2700	Normal
	s	35	25	30	8	300ml min ⁻¹
		R ₁ (10)	R ₂ (5)	(10)	(1)	
Cd	°C	100	250		2100	Normal
	s	30	30		5	300ml min ⁻¹
		R ₂	R ₂			
Cr	°C	100	200	1000	2700	Normal
	s	35	2	28	4	300ml min ⁻¹
		R ₂ (10)	(5)	R ₂ (10)	(1)	
Cu	°C	100	350	800	2600	Normal
	s	30	5	25	4	300ml min ⁻¹
		R ₂ (10)	(10)	(10)	(1)	
Pb	°C	100	250	600	2300	Normal
	s	30	12	24	5	300ml min ⁻¹
		R ₂ (10)	(5)	R ₁ (10)	(1)	
Ni	°C	100	500	1000	2700	Miniflow 4s
	s	40	5	35	5	50ml min ⁻¹
		R ₂ (10)	(5)	R ₁ (10)	(1)	
Zn	°C	100	500		2550	Miniflow 4s
	s	40	30		5	50ml min ⁻¹
		R ₁ (10)	R ₂ (10)		(1)	

R₁, R₂ - ramping rate for HGA 76

() ramp time for HGA 500

before addition of NTA and 1, 2 and 3 h afterwards. Metal concentrations in the samples were determined as described in section 3.8.2. As one surface of the specimen was covered with a silicone layer the surface contact load was 0.1486 m³ of settled sewage per m² of fibre glass, which reproduced the same surface contact load found in the settling tanks.

3.10 Evaluation of Some Methods Available for the Preservation of Condensed Phosphates in Samples of Waste Water

Primary settled sewage was collected from Hogsmill Valley Water Pollution Control Works (Thames Water Authority, U.K.). A portion of the sample was filtered through a GF/C glass microfibre filter (Whatman Labsales, Maidstone, U.K.). Presentatives were added to both filtered and unfiltered samples, at normal and elevated pH (>10). All samples were kept at 20°C. The following preservatives were used:-

- 1 - High pH. To increase the pH a solution of 5M sodium hydroxide (NaOH) was added to achieve a final pH between 10 and 10.5.
- 2 - Mercuric chloride (HgCl₂). This was added to produce a concentration of 40 mgℓ⁻¹ in the sample.
- 3 - Mercuric chloride in conjunction with elevated pH. The same solution was used as above and the pH increased by the addition of 5M NaOH to the same range as in 1.
- 4 - Formaldehyde (solution 40% V/V). 5mℓ of this solution was added to each litre of sample.
- 5 - Formaldehyde in conjunction with elevated pH. Formaldehyde was added as in 4. and the pH was increased using 5M NaOH as in 1.

All the glassware used was made of borosilicate glass. Before use the glassware was leached overnight in 5% V/V analar sulphuric acid, and rinsed several times in distilled water prior to use. Between experiments the glassware was kept in distilled water. Orthophosphate and total inorganic phosphate were determined immediately after filtration and addition of the preservative. Further determinations were undertaken after 6 days. Colorimetric method was used as described in Section 3.8.1.10.

3.11 Treatment of Data

The results obtained in the primary sedimentation and in the activated sludge pilot plant simulations were treated statistically. The paired values for each parameter or concentration were used. A t-test (Bowker and Lieberman, 1972) was performed on the means, using the differences between pairs of values, the parameters or concentration being tested at 5% level of significance.

4. RESULTS

4.1 An evaluation of mercuric chloride and formaldehyde as preservatives for condensed phosphates in primary settled sewage at normal pH and pH 10.

During the programme to be undertaken it was necessary to determine the concentration of condensed phosphates present in sewage samples. The need for this was twofold, first to determine if significant quantities of STPP were present, since it is a powerful chelator and would influence metal removal, secondly to monitor detergent phosphorus so that the "wash day" could be identified and the changes in concentration associated with this used to calculate equivalent concentrations of NTA or zeolite type A. The ideal preservative for condensed phosphates in sewage was not evident, therefore a series of experiments were undertaken to select the optimum one.

Mercuric chloride and formaldehyde were added to both filtered and unfiltered samples of primary settled sewage at normal and pH 10 as described in section 3.10. Orthophosphate and total inorganic phosphate were determined immediately after filtration and addition of the preservatives. Further determinations were undertaken on the first, third and sixth day.

The average concentration of orthophosphate and total inorganic phosphate present in both filtered and unfiltered samples and with the various preservatives, are presented in Table 14. For the results of filtered samples the mean and deviations from the means for different storage times were calculated. These data are also included in Table 14.

The average concentrations of total inorganic phosphate (orthophosphate and condensed phosphate) in the unfiltered and filtered samples, without preservative, were 7.40 mg l^{-1} as P and 5.82 mg l^{-1} as P respectively at the beginning of the experiment. Since the orthophosphate concentration at that stage was 5.26 mg l^{-1} as P for unfiltered and 4.28 mg l^{-1} as P for filtered samples, hydrolysis was expected to occur.

The results for the analysis of orthophosphate in filtered samples without preservatives, at normal pH, indicated an increase of 10.7% in the concentration of orthophosphate during the 6 days of the experiment. In the unfiltered samples from the same source an increase of 20.7% was observed. No interference was found in the blank determination using the preservatives at normal and high pH. However, when samples were treated with preservatives at high pH interference was observed as can be seen from Table 14.

Considering the mean values for each treatment, it was evident that when filtered samples were used, it was possible to rank the results in terms of the difference from the mean value, expressed in mg l^{-1} as P. The samples treated with HgCl_2 at normal pH presented the smallest difference from the mean with a range between -0.07 to +0.06. When formaldehyde was used at high pH, the range was between -0.16 to 0.00. The samples containing HgCl_2 at pH 10 showed a range from -0.15 to +0.21. A variation between -0.21 to +0.35 was found when pH was increased in the filtered samples. The use of formaldehyde at normal pH resulted in a variation from -0.25 to +0.34.

Table 14 Concentration of orthophosphate in settled sewage samples, filtered and unfiltered, with different preservatives, analysed at different times.

Sample		Orthophosphate(as P) mg l^{-1} after storage				
		0	1 day	3 days	6 days	Mean
Settled sewage	unfiltered	5.26	5.96	6.33	6.63	-
	filtered	4.28	4.20	4.48	4.74	4.43
	D.M.*	-0.15	-0.23	+0.05	+0.31	
Settled sewage pH10	unfiltered	4.19	5.35	6.04	6.44	-
	filtered	4.19	4.03	4.14	4.59	4.24
	D.M.	-0.05	-0.21	-0.10	+0.35	
Settled sewage HgCl_2	unfiltered	4.89	4.77	5.34	5.85	-
	filtered	4.09	4.16	4.14	4.24	4.16
	D.M.	-0.07	0.00	-0.02	+0.06	
Settled sewage HgCl_2 , pH ₁₀	unfiltered	5.11	5.24	5.49	5.53	-
	filtered	3.56	3.54	3.76	3.90	3.69
	D.M.	-0.13	-0.15	+0.07	+0.21	
Settled sewage Formaldehyde	unfiltered	5.00	5.52	6.20	6.48	-
	filtered	4.15	4.16	4.54	4.74	4.40
	D.M.	-0.25	-0.24	+0.14	+0.34	
Settled sewage Formaldehyde pH 10	unfiltered	5.11	5.43	5.43	5.46	-
	filtered	3.84	4.09	4.04	4.00	4.00
	D.M	-0.16	+0.09	+0.04	0.00	

*D.M. Deviation from the mean concentration in filtered samples.

The filtered sample treated with formaldehyde at normal pH exhibited an increase of 14.2% in orthophosphate concentration after 6 days. However, when the same samples were treated with formaldehyde at high pH the increase was 4.0%. Considering the differences from the mean value,

samples treated with formaldehyde at normal pH presented higher deviations from the mean, compared with those from samples when formaldehyde was used at high pH.

An experiment was undertaken to permit an estimation of the repeatability of the method, this was performed on filtered samples. Nine replicates were analysed and yielded a mean of $4.17 \text{ mg } \ell^{-1}$ of orthophosphate as P with a standard deviation of 0.14. The concentrations ranged from 3.90 to $4.32 \text{ mg } \ell^{-1}$ as P. The differences from the mean in Table 14 were compared with the value found for the standard deviation. Settled sewage treated with mercuric chloride showed results that were within the range of ± 1 standard deviation. In the other tests the results were out of the range.

From the consideration of the data above it is evident that mercuric chloride, in filtered samples, without adjustment of the pH was the most satisfactory preservative.

4.2 An investigation of the effect of NTA on metal solubilisation in raw sewage and mixed primary sludge samples in the presence or absence of spiked heavy metals

Since it is a chelating agent, NTA will compete with the other natural ligands present in sewage to bind with the metals present. This competition, as any chemical equilibrium, will be dependent on several factors including, concentration of ligands concentration of the metals and form (soluble or insoluble) of the metal and the ligands.

During experiments to be undertaken in this programme two concentrations of heavy metals were to be studied. The naturally occurring concentration (low) and a "high" concentration achieved by the addition of a solution of heavy metal salts. It is often suggested that "spiked" metal is more readily available than the indigenous metal and that the behaviour of spiked metals is atypical. So that the applicability of subsequent experiments to natural high heavy metal concentrations could be ascertained, a number of jar tests were undertaken to determine the availability of indigenous and spiked heavy metals to NTA.

Raw sewage and mixed primary sludge samples spiked or not with heavy metals were shaken with NTA in borosilicate stoppered flasks

placed inside a temperature-controlled water bath as described in section 3.7. The same procedure was adopted for control samples without NTA. Aliquots were withdrawn for metal determinations (total and soluble) before the shaking period and at several intervals during shaking.

To study the effect of NTA on metal mobilization, the percentage of metal in the soluble fraction was determined in both control and test samples. Ultracentrifugation was used to isolate the soluble fraction from the solids. Percentage mobilizations were calculated as follows:

$$\text{Percentage Mobilization} = \frac{C_{st} - C_{sc}}{C_i} \times 100$$

where C_{st} = concentration of metal in test supernatant

C_{sc} = concentration of metal in control supernatant

C_i = concentration of total metal in the sample.

Percentage Mobilization can be calculated by subtracting the percentage of metal in control supernatant from the percentage of metal in test supernatant or,

$$\text{Percentage Mobilization} = \frac{C_{st}}{C_i} \times 100 - \frac{C_{sc}}{C_i} \times 100$$

4.2.1. Effect of NTA on metal mobilization in raw sewage spiked or not with metal solutions

Metal analyses were carried out on supernatants prepared from samples collected from the flasks in the shaking water bath at the intervals of 0.5, 0.8, 1.4, 2.2, 3 and 4 h. The results are presented graphically in Fig. 4. The percentage of metals present in the supernatant at the end of the 4 h shaking period were calculated and are summarised in Table 15.

All indigenous metals in the raw sewage were mobilized in the presence of NTA with copper, cadmium and lead showing the largest mobilization. NTA solubilised all the nickel and zinc present in insoluble forms, whilst chromium was mobilized only slightly.

During the jar test in the absence of NTA no variation in the concentration of soluble metal was observed which suggested an equilibrium existed between different metals and ligands which was unaffected by the shaking.

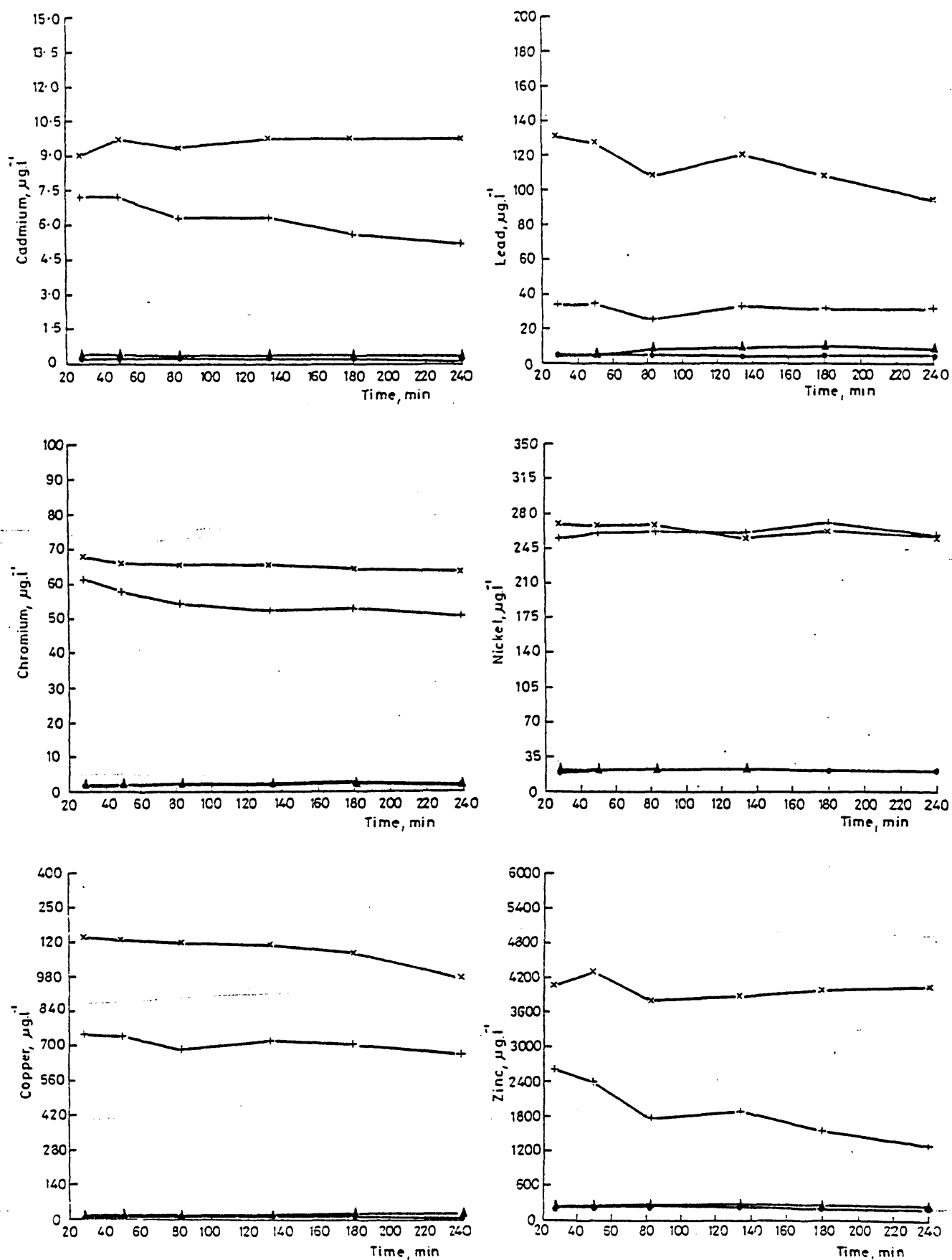


Figure 4 Concentration of heavy metals in supernatants of raw sewage (—●—) in the presence of NTA (—▲—) and in supernatants of raw sewage spiked with metal (—+—) in the presence of NTA (—×—).

Table 15 - Effect of NTA on metal mobilization during jar tests on raw sewage in the presence or absence of spiked metal solutions.

Metal	Raw sewage				Raw sewage spiked with metals			
	Total metal conc. $\mu\text{g l}^{-1}$	Percentage in supernatant		% Mobilization	Total metal conc. $\mu\text{g l}^{-1}$	Percentage in supernatant		% Mobilization
		Control	Test			Control	Test	
Cadmium	0.40	49	98	49	12.5	42	78	36
Chromium	4.36	43	47	4	69.0	73	92	19
Copper	40.0	25	83	58	3360	20	29	9
Lead	11.5	40	72	32	321	10	29	19
Nickel	21.6	96	100	4	256	100	100	0
Zinc	279	82	100	18	5960	22	68	46

At high metal concentrations (i.e. when raw sewage was spiked with metals) the equilibrium conditions changed and a decrease in metal concentration in the supernatant during the shaking was observed, except for nickel and lead which were constant. Zinc exhibited the greatest reduction varying from $2,600 \mu\text{g l}^{-1}$ to $1,320 \mu\text{g l}^{-1}$ in samples collected at 0.5 and 4.0 h, respectively. For cadmium, chromium, copper and zinc a faster removal during the first 1.4 h of shaking was observed.

In the presence of NTA, the percentage of metals present in the supernatant were higher than the control since NTA formed soluble complexes with the metals. No mobilization of nickel was observed since all the nickel originally present was in a soluble form. As can be seen in Table 15 zinc had the highest percentage mobilization (46%) followed by cadmium (36%), chromium and lead (19%) and copper (9%).

From this experiment it may be concluded that zinc and chromium in this particular system formed strong complexes with NTA which prevent the formation of insoluble compounds. However cadmium, copper and lead tended to remain insoluble even in the presence of NTA which suggested the formation of very strong insoluble metal compounds. As nickel appeared in a completely soluble form during the experiment with spiked metals it was not possible to form a conclusion about its behaviour in the presence of NTA, but from the experiment with raw sewage without metals it was apparent that nickel formed a stronger complex with NTA than with the insoluble natural ligands.

4.2.2 Effect of NTA on metal mobilization in mixed primary sludge spiked or not with metal solution

Supernatants were prepared from samples collected at intervals of 0.35, 0.68, 1.3, 2 and 3 h, and used for metal analysis. The results are presented in Fig. 5. In Table 16 the percentages of metal present in the supernatant after 3 h shaking are presented.

NTA mobilized all metals from the mixed primary sludge except chromium for which no mobilization was observed, nickel showed the largest mobilization (17.3%). For the other metals the mobilizations were smaller with 1.6% for cadmium, 1.9% for zinc and 2.0% for lead.

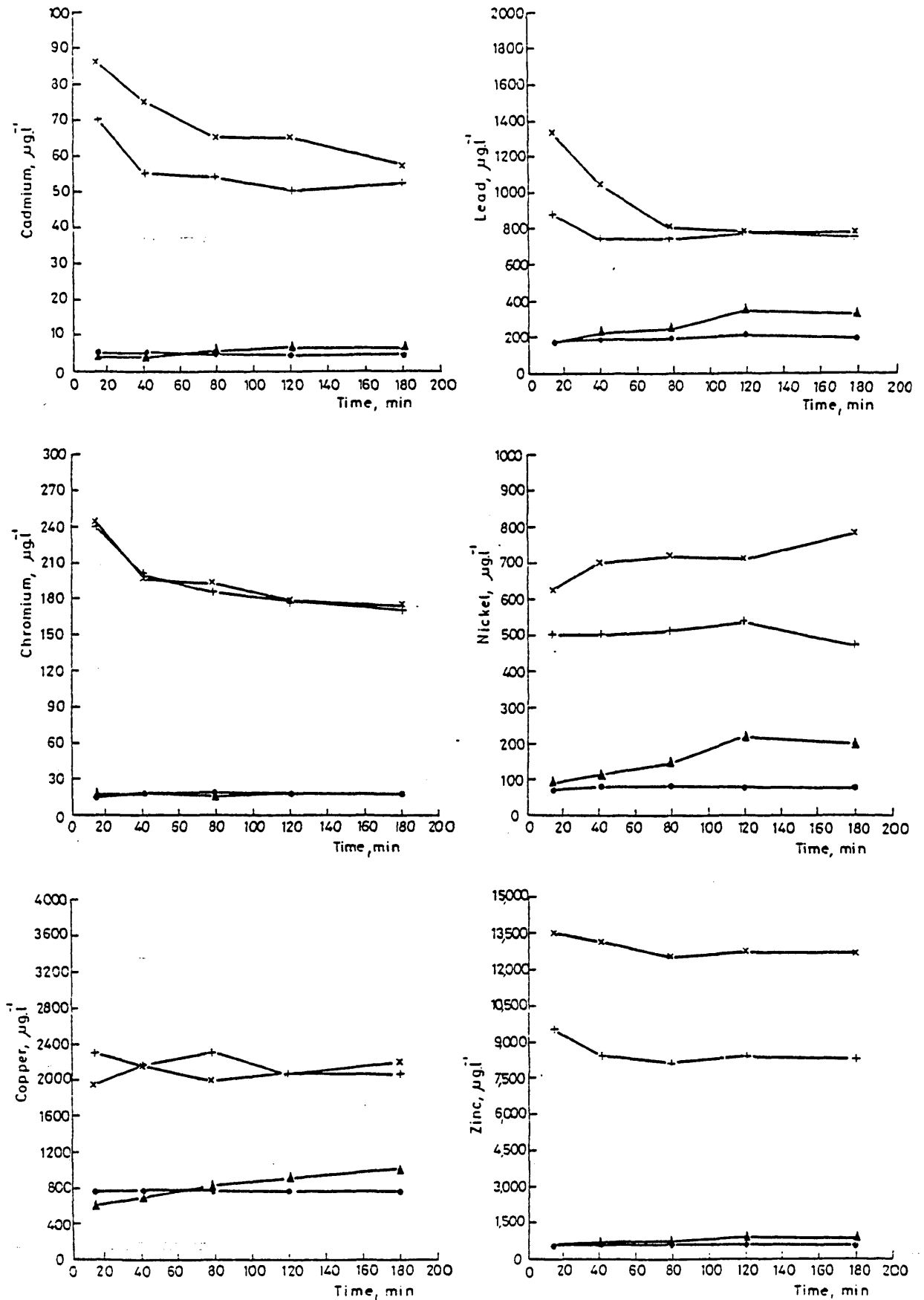


Figure 5 Concentration of heavy metals in supernatant of mixed primary sludge (---●---) in the presence of NTA (—▲—) and in supernatants of mixed primary sludge spiked with metal (—+—) in the presence of NTA (—×—).

Table 16 - Effect of NTA on metal mobilization during jar tests on mixed primary sludge in the presence or absence of spiked metal solutions

Metal	Mixed primary sludge				Mixed primary sludge spiked with metals			
	Total metal conc. mg l^{-1}	Percentage in supernatant		% Mobilization	Total metal conc. mg l^{-1}	Percentage in supernatant		% Mobilization
		Control	Test			Control	Test	
Cadmium	0.120	3.7	5.3	1.6	0.596	8.7	9.6	0.9
Chromium	0.364	4.8	4.8	0.0	1.390	12.2	12.4	0.2
Copper	14.850	5.1	6.8	1.7	26.370	7.9	8.2	0.3
Lead	6.683	2.8	4.8	2.0	26.370	2.8	2.9	0.1
Nickel	0.709	10.9	28.2	17.3	1.762	26.7	44.3	17.6
Zinc	14.000	4.1	6.0	1.9	49.860	16.6	25.4	8.8

The presence of high concentrations of organics in the sludge, in conjunction with a low concentration of NTA possibly explains the ability of sludge to bind metals. An equilibrium between soluble and insoluble forms of cadmium, lead, nickel and zinc was established after 2 h of shaking, however, for copper no equilibrium occurred during the 3 h of experiment. For mixed primary sludge in the absence of NTA the concentration of metal in the supernatant remained constant which indicates that the system was in equilibrium and unaffected by shaking. When metals were added, a new system was formed. In the experiment in the absence of NTA a reduction in the metals in the supernatant occurred except for nickel. It may be concluded that insoluble compounds were formed.

In the presence of NTA all metals were mobilized from the sludge with the exception of chromium. Throughout the shaking the concentration of metals in the supernatant changed and after 3 h the percentage mobilization indicated high mobilization for nickel (17.6%). Zinc mobilization was 8.8% followed by cadmium (0.9%), copper (0.3%), chromium (0.2%) and lead (0.1%).

From the above it is evident that zinc and to a lesser extent nickel and chromium formed stronger complexes with NTA than with natural insoluble ligands and the other metals (i.e. copper, cadmium and lead) exhibit a tendency to form insoluble compounds in this matrix.

4.3 Evaluation of the hydraulic similarity of the two primary sedimentation tanks

The use of one primary sedimentation tank as a control requires that both tanks should have the same hydraulic conditions thus any effect observed would be due to the presence of builder in the test tank. The main objective of this experiment was to determine if any change in the influent quality was reflected at the same time and in the same intensity in both tanks. It was also intended during this experiment to assess the efficiency and comparability of the two sampling systems.

The hydraulic similarity of the two plants was determined as described in section 3.6.1 by introducing sodium chloride in the inlet of the sedimentation tanks and measuring its concentration in effluent samples collected by using the automatic sampling system manually and also in grab samples collected at the same time. Experiments were

undertaken with the plants operating at 1 and 3 DWF. The results for influent and effluent chloride concentrations are presented in Figs. 6 and 7.

The background chloride concentration was monitored throughout the experiment with the same frequency as for the effluents and mean values of 44 and 45 mg ℓ^{-1} as Cl^- were found for 1 and 3 DWF, respectively.

No difference was found in the results from samples collected at the same time using the sampling system or as grab samples. It may be concluded that the residual samples in the sampling tube from previous samples did not adversely affect the following sample. The difference in the effluent chloride concentration between control and test in the experiment at 1 DWF, during the peak can be estimated from Fig. 6 to be 4 mg ℓ^{-1} as Cl^- . Comparing this result with the amount of chloride injected in the system (84.9 g Cl^-) it may be concluded that any increase in metal concentration in the influent of the tanks would produce peaks with comparable intensities in both effluents at the same time. The results in Fig. 7 indicate a difference in chloride concentration in the effluent during the peak of 3 mg ℓ^{-1} and the same conclusion may be drawn.

4.4 Metal removal during the primary sedimentation process

The objective of this work was to determine the fate of the two detergent builders, zeolite type A and NTA, during primary sedimentation and to assess their effect on heavy metal removal. To achieve this twelve paired experiments were undertaken, using a test pilot plant to which the builders were added and a control; three hydraulic conditions were used 1 DWF, 3 DWF and variable flow. The data for metal removal from the control plant during these twelve experiments have been tabulated and treated separately to permit the removal of metals alone to be evaluated. Necessarily these control data are repeated in section 4.5 and section 4.6 for comparative purposes.

4.4.1 The influence of influent heavy metal concentrations on their behaviour in primary sedimentation

A total of twelve experiments to study heavy metal removal in the primary sedimentation pilot plant were undertaken during a period of four months. During this time wide variations in the concentrations of

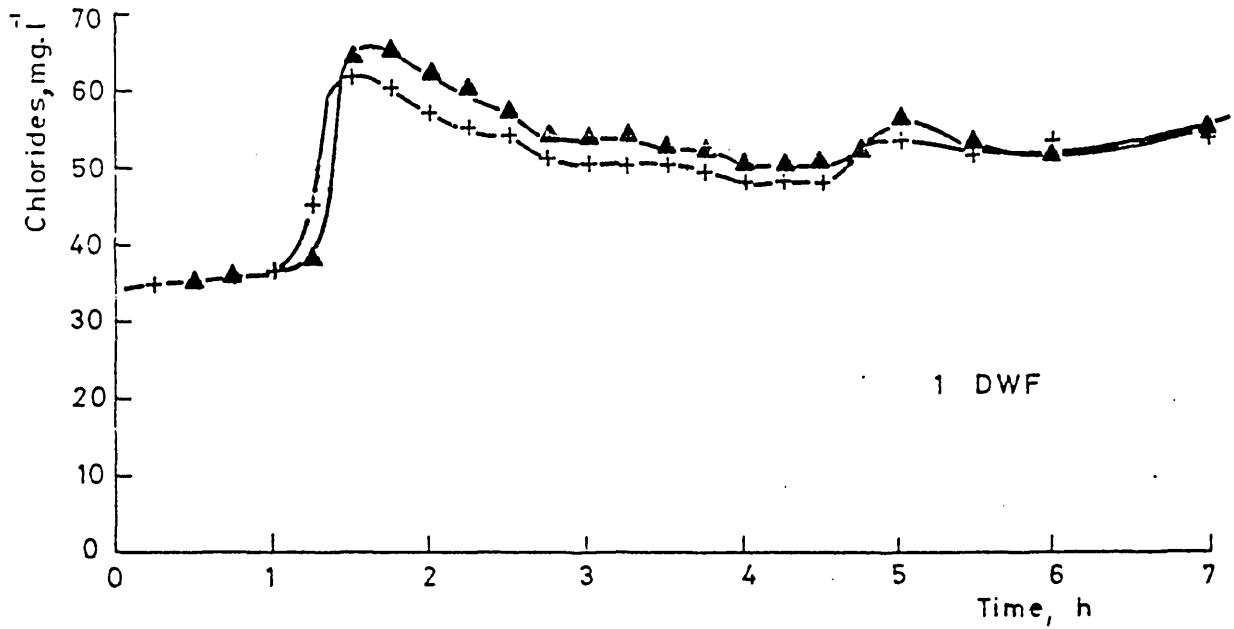


Figure 6 - Chloride concentrations in effluent control (—▲—) and effluent test (---+---) in primary sedimentation pilot plant at 1 DWF, due to a spike of sodium chloride.

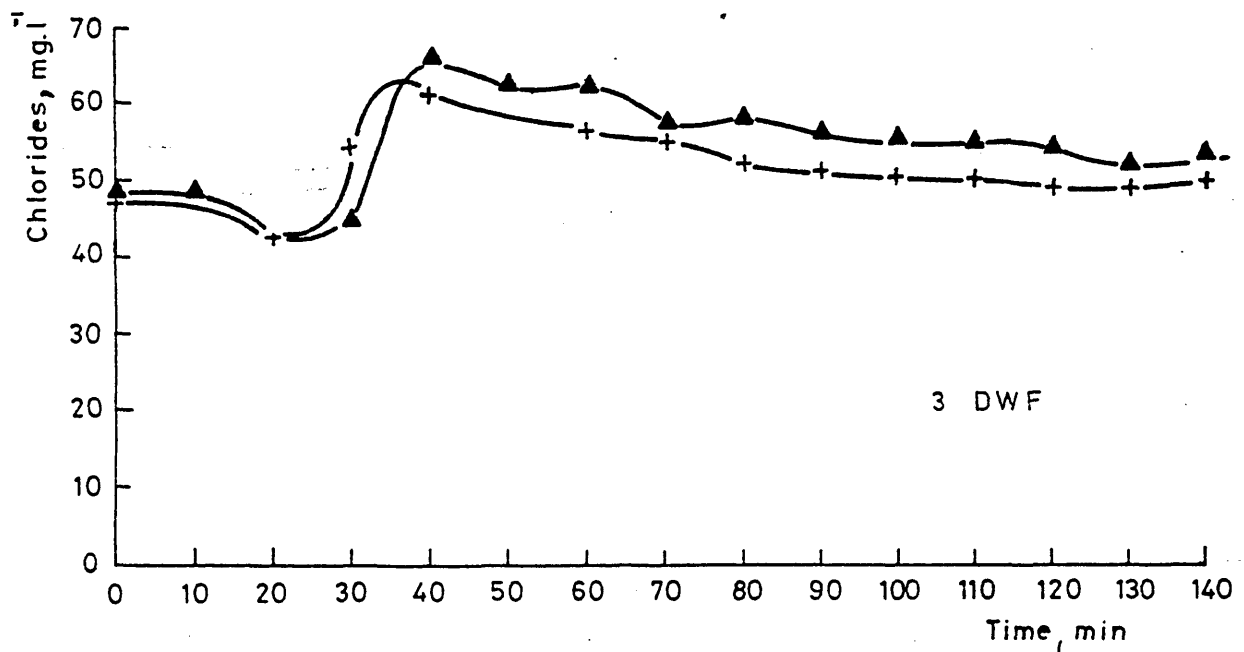


Figure 7 - Chloride concentration in effluent control (—▲—) and effluent test (---+---) in primary sedimentation pilot plant at 3 DWF, due to a spike of sodium chloride.

heavy metals in the raw sewage occurred. Moreover, the daily flow to the Hogsmill Works also varied, mainly due to weather conditions. Although the adjustable weir and offset cam assembly permitted the simulation of normal, heavy and variable flow to the pilot scale sedimentation tanks, it was not possible to simulate the changes in the nature of the sewage which occur as the result of storm conditions and other factors which affect the flow. Therefore, the total flow of sewage to the Hogsmill Works was recorded during each experiment and the concentrations of heavy metals were determined every 3 h. These parameters are shown in Fig. 8 for a typical instance of normal flow and Fig. 9 for elevated flow conditions.

During the normal variations in flow the data in Fig. 8 indicate that for cadmium, copper and zinc, in particular, the concentrations increased with decreasing flow, possibly because at higher flows the metal concentrations were subject to some dilution. The highest concentration of lead appeared in a shorter time after the daily peak flow, possibly reflecting the transport of larger quantities of lead from scouring and road run off. At the onset of storm conditions (Fig. 9) the peak lead concentration in raw sewage was similar to that which occurred during normal flow. However, the concentration of lead decreased steadily thereafter, indicating that the lead may have entered the works in a transient peak arising from run off and scouring. The large initial peaks of cadmium and nickel may also have been caused by the same phenomenon. The influent concentration of copper also exhibited a marked increase towards the end of the storm period. This may have been a result of the return to the flow of the sewage which had been previously retained in the storm tanks.

As a result of these factors, the mean concentrations of heavy metals, suspended solids and COD in the influent raw sewage and the settled sewage for each three day experiment varied widely. These mean concentrations are shown in Table 17. The range of heavy metal concentrations during the entire experimental period were, cadmium $0.37 - 2.07 \mu\text{g l}^{-1}$, chromium $7.8 - 36.3 \mu\text{g l}^{-1}$, copper $57 - 267 \mu\text{g l}^{-1}$, lead $29 - 117 \mu\text{g l}^{-1}$, nickel $6.3 - 22 \mu\text{g l}^{-1}$ and zinc $105 - 314 \mu\text{g l}^{-1}$. From comparison of the heavy metal concentrations in Table 17 with the removal efficiencies presented in Tables 18 to 20 it appeared that heavy metal removal was not influenced by the influent concentration. Moreover the mean heavy metal concentrations in the raw sewage over each 3 day period were apparently unaffected by the flow to the Works. These

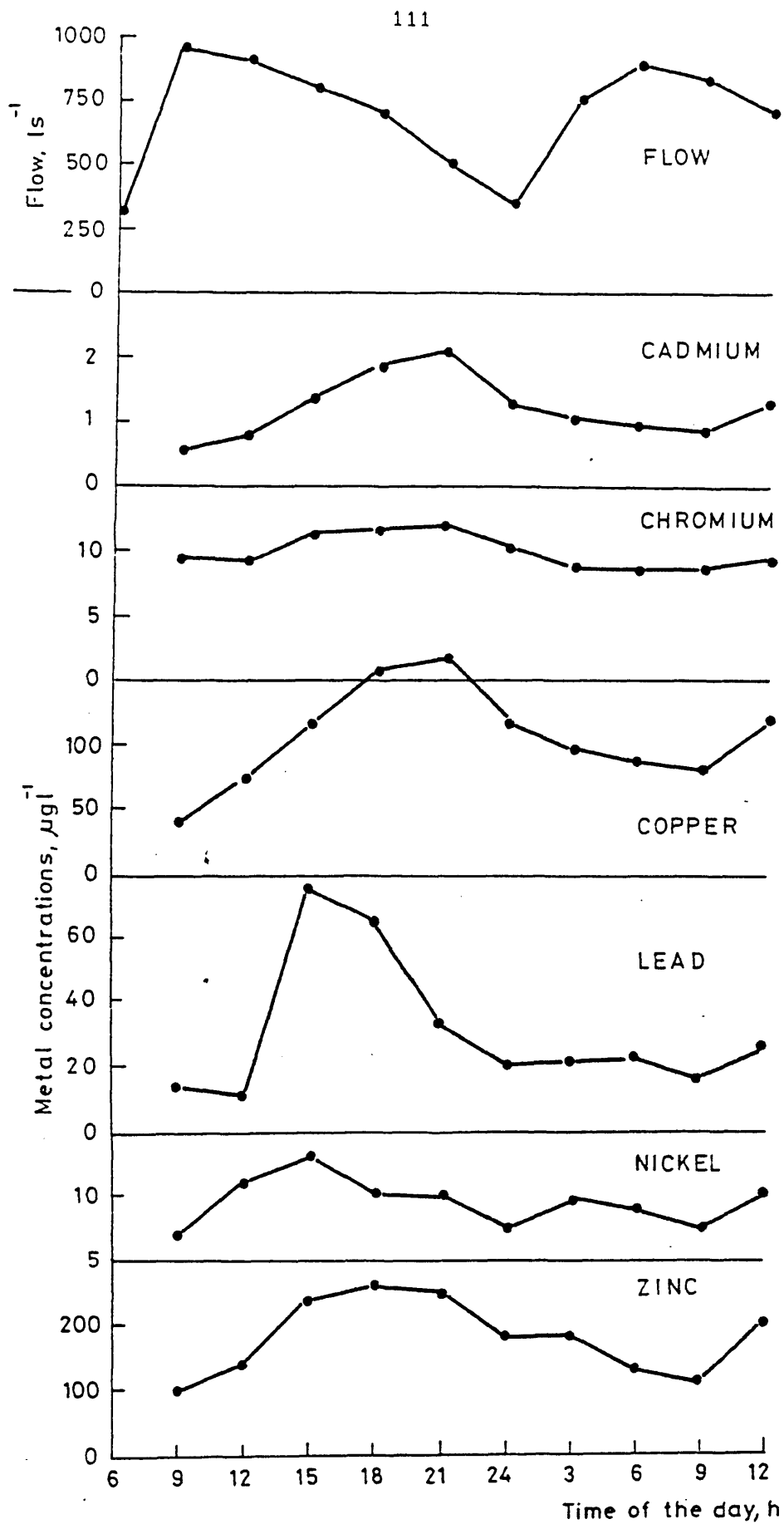


Figure 8 - Variations on the flow to the Hogsmill Valley Sewage Treatment Works and mean concentrations of heavy metals in raw sewage during typical "normal flow" conditions

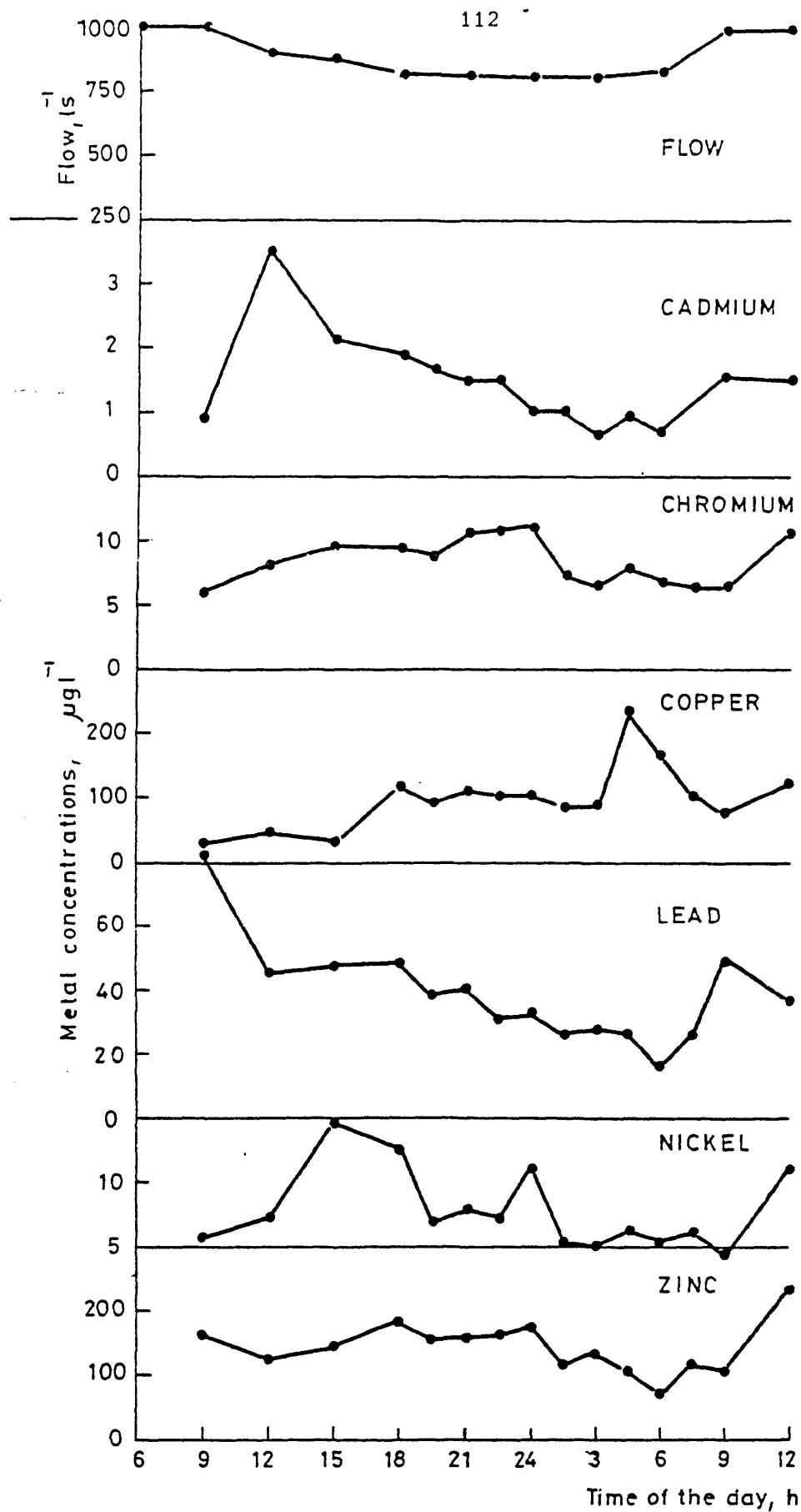


Figure 9 - Variations on the flow to the Hogsmill Valley Sewage Treatment Works and mean concentrations of heavy metals in raw sewage during "storm flow" conditions.

Table 17 - Mean Concentrations of heavy metals, suspended solids and COD in raw and settled sewage

Flow			Concentration*															
			Cadmium		Chromium		Copper		Lead		Nickel		Zinc		SS		COD	
Pilot Plant		Works	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF	INF	EFF
1 DWF	<	1 DWF	0.37	0.27	7.8	5.9	70	43	31	26	8.7	7.4	145	116	274	172	374	295
	<	1 DWF	2.07	1.43	36	30	267	117	52	27	12	15	314	140	251	131	370	210
		1 DWF	1.58	0.87	9.9	6.7	158	79	117	106	10	7.0	185	127	262	136	362	272
		1 DWF	-	-	17	11	110	51	45	17	22	16	256	188	322	162	495	318
3 DWF	<	1 DWF	1.92	1.60	36	28	133	100	54	29	9.5	7.6	209	163	458	164	646	330
		1 DWF	1.24	1.03	11	8.8	110	102	31	14	10	7.0	184	131	391	134	454	259
		1 DWF	0.72	0.66	11	8.3	118	75	36	18	15	12	184	161	309	157	410	241
	>	1 DWF	0.64	0.30	25	17	100	40	38	13	7.5	4.6	151	84	393	162	471	246
Variable Flow	<	1 DWF	0.86	0.81	14	13	57	49	29	22	6.9	6.5	105	80	224	143	-	-
		1 DWF	0.70	0.70	9.2	8.4	102	84	45	43	20	19	237	222	155	121	-	-
		1 DWF	1.05	0.80	8.8	7.0	65	44	32	21	6.3	5.9	170	126	190	133	-	-
	>>	1 DWF	1.44	1.03	8.5	6.9	100	49	38	22	7.8	7.5	145	119	146	67	-	-

* Concentrations for metals are in $\mu\text{g } \ell^{-1}$ and for SS and COD are in $\text{mg } \ell^{-1}$

Table 18 - Percentage removals of heavy metals and suspended solids in primary sedimentation calculated from samples of raw and settled sewage taken every 3 h for 27 h.

Flow		% Removal						
Pilot Plant	Works	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	SS
1 DWF	< 1 DWF	29	25	36	16	15	36	37
	< 1 DWF	31	15	56	48	120	55	48
	1 DWF	45	32	50	10	28	32	48
	1 DWF	-	33	54	63	27	26	50
Mean		35	26	49	34	12	37	46
3 DWF	< 1 DWF	17	23	24	47	20	22	64
	1 DWF	17	17	7	56	30	28	66
	1 DWF	8	22	57	50	18	12	47
	> 1 DWF	52	34	57	65	39	44	59
Mean		23	24	36	54	27	27	59
Variable Flow	< 1 DWF	3	3	18	24	7	23	44
	1 DWF	5	12	19	4	5	7	22
	1 DWF	26	24	33	34	14	26	30
	>> 1 DWF	30	11	40	35	3	30	51
Mean		16	12	27	24	7	19	39

Table 19 - Percentage removals of heavy metals, suspended solids and COD in primary sedimentation calculated from composites of raw and settled sewage.

Flow		% Removal							
Pilot Plant	Works	Cadmium	Chromium	Copper	Lead	Nickel	Zinc	SS	COD
1 DWF	< 1 DWF	55	41	51	45	9	59	32	22
	< 1 DWF	21	9	53	52	56	50	44	43
	1 DWF	62	38	43	10	30	49	48	25
	1 DWF	-	21	57	53	12	11	45	36
Mean		46	27	51	40	27	42	42	32
3 DWF	< 1 DWF	57	31	26	65	29	48	76	49
	1 DWF	31	39	32	62	46	49	67	43
	1 DWF	57	26	50	33	16	11	56	41
	> 1 DWF	-	49	60	43	34	50	54	48
Mean		48	36	42	51	31	39	63	45

Table 20 - Percentage removals of heavy metals in primary sedimentation calculated from composites of raw sewage and primary sludge and mass balances for heavy metals

Flow		Parameter											
Pilot Plant	Works	Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
		Removal	Mass	Removal	Mass	Removal	Mass	Removal	Mass	Removal	Mass	Removal	Mass
		%	Balance %	%	Balance %	%	Balance %	%	Balance %	%	Balance %	%	Balance %
1 DWF	< 1 DWF	64	91	63	82	100	67	120	57	35	80	40	123
	< 1 DWF	47	81	46	73	33	124	107	64	51	48	40	111
	1 DWF	35	140	25	114	39	104	63	65	33	97	45	104
	1 DWF	-	-	17	104	81	81	102	67	43	77	48	73
Mean		49		38		63		98		40		43	
3 DWF	< 1 DWF	21	156	18	116	23	103	45	124	20	111	13	153
	< 1 DWF	14	120	30	110	22	111	55	108	26	125	34	118
	1 DWF	14	176	67	71	86	73	174	41	8	108	39	78
	1 DWF	72	96	62	88	72	90	150	48	29	105	52	98
Mean		30		44		51		105		21		34	

observations indicate that the variations in influent heavy metal concentrations and heavy metal removal may have been due to a variety of complex factors.

4.4.2 The influence of flow conditions on heavy metal removal efficiencies.

Heavy metal removal efficiencies were determined during conditions designed to simulate a normal dry weather flow (1 DWF), elevated flow (3 DWF) and variable flow during dry weather conditions. Experiments were replicated four times for each flow condition. Metal removal has been calculated by three methods, method 1 based on the average values for influent and effluent concentrations determined from the 3 h samples, method 2 using the concentrations retained by the sludge solids in the tank and the concentrations in the influent composite sample collected during all three days of the experiment and method 3 using the values for influent and effluent concentrations determined from composite samples collected throughout the experiment. Mass balances were also calculated for each metal using influent and effluent composite samples and concentrations of metal retained in the tank during the three day experiments. Methods of calculating removals and mass balances are presented in Appendix IV.

Suspended solids in the influent and effluent of the control and test plant were determined by filtration. The average values for suspended solids in the influent and effluents were calculated from the values determined at three hourly intervals and percentages removals were calculated from these. The variable flow experiment was not immediately amenable to this type of treatment. To permit the percentage removal to be determined it was necessary to calculate the average influent suspended solids and the average effluent suspended solids. this was undertaken nine times at 3 h intervals. Thus three flow rates determined at hourly intervals were averaged as were the pairs of influent and effluent suspended solids values which were separated by an interval of 3 h. The 9 influent and effluent values obtained were then used to calculate the 27 h average values, these in turn were used to calculate percentage removal,

$$\text{Percentage Removal} = \frac{(\text{average influent SS} - \text{average effluent SS})}{\text{average influent SS}} \times 100$$

A similar calculation was adopted for average metal concentration during variable flow experiments.

Heavy metal, suspended solids and COD removal efficiencies calculated using samples taken every 3 h, (method 1) and composite samples (method 3) are shown in Tables 18 and 19 respectively. Removal efficiencies calculated from method 2 are shown in Table 20, together with the mass balances of heavy metals through primary sedimentation. Removal efficiencies for variable flow conditions are not shown in Tables 19 and 20 because of difficulties in matching discrete sample volumes to the variations in flow.

A general trend in the relative efficiencies of heavy metal removal was obtained by calculating the mean removals for all twelve experiments. The removal efficiencies calculated from the three hourly samples shown in Table 18 were copper and lead, 37%, zinc, 28%, cadmium, 24%, chromium, 21% and nickel, 19%. Copper and lead also had the highest recorded removals in individual experiments of 57% and 65% respectively, while the lowest nickel removal was only 3%.

Although there were considerable variations in heavy metal removal efficiency during each of the three flow conditions studied, the mean values shown in Table 18 exhibited some positive trends. The removals of cadmium, chromium, copper and zinc were highest during normal dry weather flow conditions, lower when the flow was increased threefold and poorest during variable flow conditions. Nickel removals did not follow the same trend, although the poorest removals occurred during variable flow. Suspended solids removals did not appear to be related to the hydraulic loading however some correlation was found between influent suspended solids and percentage removal. The removal of lead which did not behave in the same way as the other elements, appeared to be related to the suspended solids removal, indicating that the lead may have been in a predominantly insoluble form.

Heavy metal removals based on composite samples, shown in Table 19, are not concordant with those presented in Table 18. Although the removal efficiencies calculated from the two types of sample were broadly similar under normal flow conditions, at elevated flow the removal efficiencies in Table 19 were higher, and did not indicate any

influence of flow on removal. The suspended solids removals determined from composite samples at elevated flows were substantially higher than at normal flows, and the removal of lead may have been influenced by this factor, with improved lead removal at increasing suspended solids removals.

The mass balances of heavy metals through primary sedimentation and the percentage removals calculated from heavy metal concentrations in primary sludge are shown in Table 20. In general, the removals under normal flow were higher than those during elevated flow conditions, with the exception of copper and lead. The mean removal efficiencies were slightly higher than those presented in Table 18, but the removals in individual experiments varied widely, with the possible exception of nickel and zinc. There were six recorded instances of removal efficiencies of 100% or greater. An examination of the corresponding mass balances indicates that these figures were obtained from experiments where the mass balances were poor. Mass balances for lead were the poorest observed, while those for chromium and nickel were generally the closest to 100%. The mass balances for lead indicate that the concentrations determined in the raw sewage were generally lower than the actual concentrations entering the pilot plant, suggesting that much of the lead in the raw sewage entered the pilot plant in peaks of short duration, while the influent concentrations of chromium and nickel were probably less variable. The data in Figs. 8 and 9 also indicate that fluctuations in the influent lead concentration were more marked than in the case of chromium and nickel. Relatively poor mass balances were occasionally observed for cadmium, copper and zinc, suggesting that these metals may sometimes be present in raw sewage in the form of transient spikes.

Due to the possible occurrence of transient fluctuations in heavy metal concentrations in raw sewage some errors would be involved in the determination of removal efficiencies if peak concentrations were not detected. The most representative determinations carried out in this study were probably those on the primary sludge, since all of this material was recovered at the end of each experiment (see below). However, the accompanying mass balances indicate that in several experiments the percentage removals shown in Table 20 were probably higher than those which actually occurred.

The results shown in Tables 18 and 20 indicate that with the exception of nickel and lead, an increase in the flow rate of raw sewage or the occurrence of variable flow would result in lower heavy metal removal efficiencies.

4.4.3 The influence of sludge solids on metal removal

In order to further investigate the significance of particulate forms of heavy metals in primary sedimentation the association of heavy metals with sludge solids was determined. Since it was not possible to take representative samples of primary sludge during the three day experiments, due to zonal sedimentation and adhesion of solids to the side of the tank, analyses were undertaken on the entire contents of the tank after the termination of each experiment. Thus, it was possible to recover all of the sludge solids from the tank. Although the primary sludge was diluted as a result of this method of sampling the concentrations of metals contributed by the settled sewage in the tank were very small compared to the concentrations in the sludge.

The concentration of heavy metals and total, volatile and non-volatile suspended solids, are shown in Table 21. Correlations of metal concentrations with the concentrations of the solids fractions are also shown in Table 21. Volatile solids were the most predominant solids fraction in the primary sludge, comprising between 79% and 88% of the total. However, despite a relatively constant composition of sludge solids, cadmium, chromium and lead concentrations in the sludge did not correlate well with the total solids concentrations. In contrast, copper, nickel and zinc were fairly well correlated with total solids in the experiments under normal flow conditions, but poor correlations were observed for all metals during increased flow.

Under normal flow conditions close correlations between cadmium, chromium, copper, lead and zinc and the non-volatile solids fraction were observed, possibly indicating that the particulate forms of these metals were predominantly inorganic in nature. In contrast, the nickel concentrations in primary sludge correlated more closely with the volatile solids concentration, suggesting the presence of organic forms of the metal. Under conditions corresponding to three times the normal dry weather flow cadmium, chromium, copper,

Table 21 - Correlations of heavy metals concentrations in primary sludge with volatile and non-volatile solids.

Flow		Concentration (mg ℓ^{-1})								
Pilot Plant	Works	SS	VSS	NVSS	Cd	Cr	Cu	Ni	Pb	Zn
1 DWF	1 DWF	3175	2729	446	-	0.136	2.11	0.182	0.962	2.39
	1 DWF	2609	2271	338	0.011	0.098	1.18	0.065	0.943	1.53
	<1 DWF	3113	2689	424	0.008	0.130	2.13	0.089	0.938	2.09
	<1 DWF	2932	2422	510	0.020	0.311	1.96	0.093	1.24	2.37
	r SS	-	0.96	0.60	0.03	0.11	0.96	0.73	0.08	0.83
	r VSS	-	-	-	0.35	0.15	0.35	0.73	0.80	0.67
	r NVSS	-	-	-	0.75	0.86	0.76	0.37	0.78	0.92
	1 DWF	9714	7914	1800	0.009	0.37	5.46	0.08	2.89	5.26
	<1 DWF	8926	7895	1067	0.041	0.41	3.94	0.20	1.36	5.01
	>1 DWF	10355	8180	2175	0.015	0.98	6.24	0.12	4.28	8.09
3 DWF	1 DWF	11355	9944	1411	0.027	0.40	2.00	0.12	2.67	2.74
	r SS	-	0.88	0.30	0.28	0.06	0.73	0.49	0.38	0.32
	r VSS	-	-	-	0.13	0.26	0.80	0.16	0.38	0.68
	r NVSS	-	-	-	0.87	0.66	0.73	0.71	0.59	0.71

r = correlation coefficient

lead and zinc concentrations again correlated most closely with the non-volatile solids fraction; in addition nickel also appeared to be associated with the inorganic fraction, unlike its behaviour in the normal dry weather flow experiments. Since the flows to the Works during the four experiments at each of the two experimental flow rates were similar, the marked change in the association of nickel with the solids fractions may have been due to the change in flow rate and may have been a result of the loss of buoyant particles when the flow rate exceeded the nominal "design" value.

4.5 Behaviour of zeolite type A during primary sedimentation at different hydraulic loadings and influent zeolite type A concentrations

4.5.1 The removal of zeolite type A during primary sedimentation

Six experiments were undertaken to determine the removal of zeolite during primary sedimentation. Two influent concentrations of zeolite were selected, 30 and 60 mg ℓ^{-1} , and three hydraulic conditions, 1 DWF, 3 DWF and variable flow. The flow conditions used for variable flow experiments are presented in Fig 10. Weather conditions, variation in the flow to the Works and sewage temperature (maximum and minimum) were recorded throughout the experiments and are presented in Figs. 11 and 12.

Suspended solids in the influent and effluent of the control and test plants were determined by filtration using glass fibre filter papers to permit the efficiency of treatment to be calculated. The glass fibre filter papers used are claimed to remove particles larger than 1.5 μm and would, therefore, remove 99% of the zeolite added to the test plant influent sewage. Thus influent suspended solids to the test pilot plant were calculated by adding the concentration of zeolite actually added to the influent sewage to the influent suspended solid values. Percentage removals were calculated by method 1 (see Appendix IV) and average values for suspended solids in the influent and effluents during variable flow experiments were calculated by the same manner as described in section 4.4.2. The results are presented in Table 22.

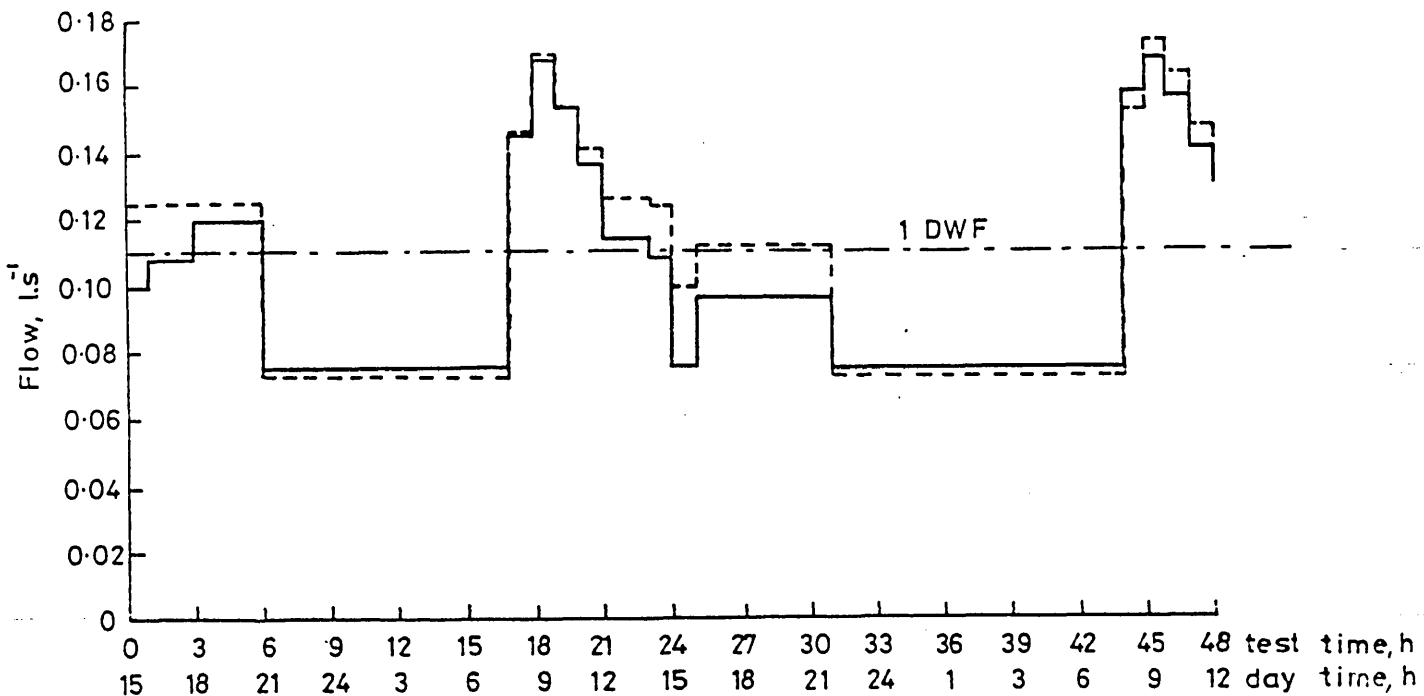


Figure 10 - Flow during zeolite type A experiments under variable flow conditions (— zeolite concentration 30 mg l^{-1} ; --- zeolite concentration 60 mg l^{-1})

Examination of Table 22 indicates that the highest percentage solids removal occurred when the influent suspended solids were highest and that the trend was reflected in all the results presented. The maximum variation between the test and control plants was 3% and not consistently in favour of one plant or the other indicating that zeolite had no significant effect on suspended solids removal. There was also a consistent relationship between influent suspended solids and influent COD, the highest values of each being present in the same influent sewage. The percentage COD removal was not determined under variable flow conditions, but at 1 DWF and 3 DWF, the maximum difference between control and test plants was 3% with no significant trend indicating that zeolite had no significant effect on COD removal.

During both experiments at 1 DWF the flow to the works was normal (approximately 1 DWF) whilst during both experiments at variable flow the works was receiving elevated flows and the storm tanks were in operation. Thus the influent suspended solids observed in the experiments at 1 DWF

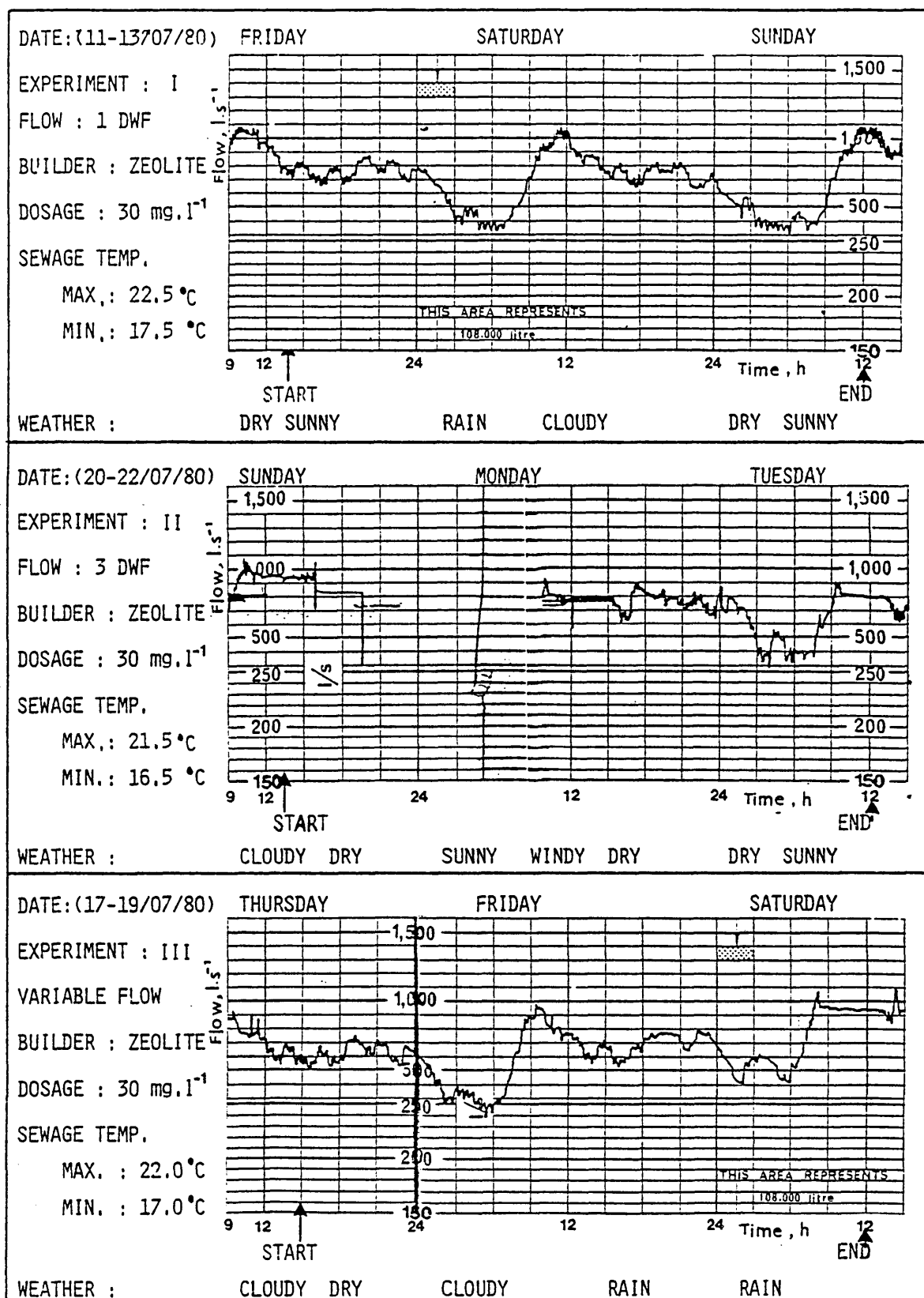


Figure 11 - Flow record from Hogsmill Valley Sewage Treatment Works, maximum and minimum temperature for sewage and weather conditions during experiments at 1 DWF, 3 DWF and Variable flow when zeolite type A was added at 30 mg l⁻¹.

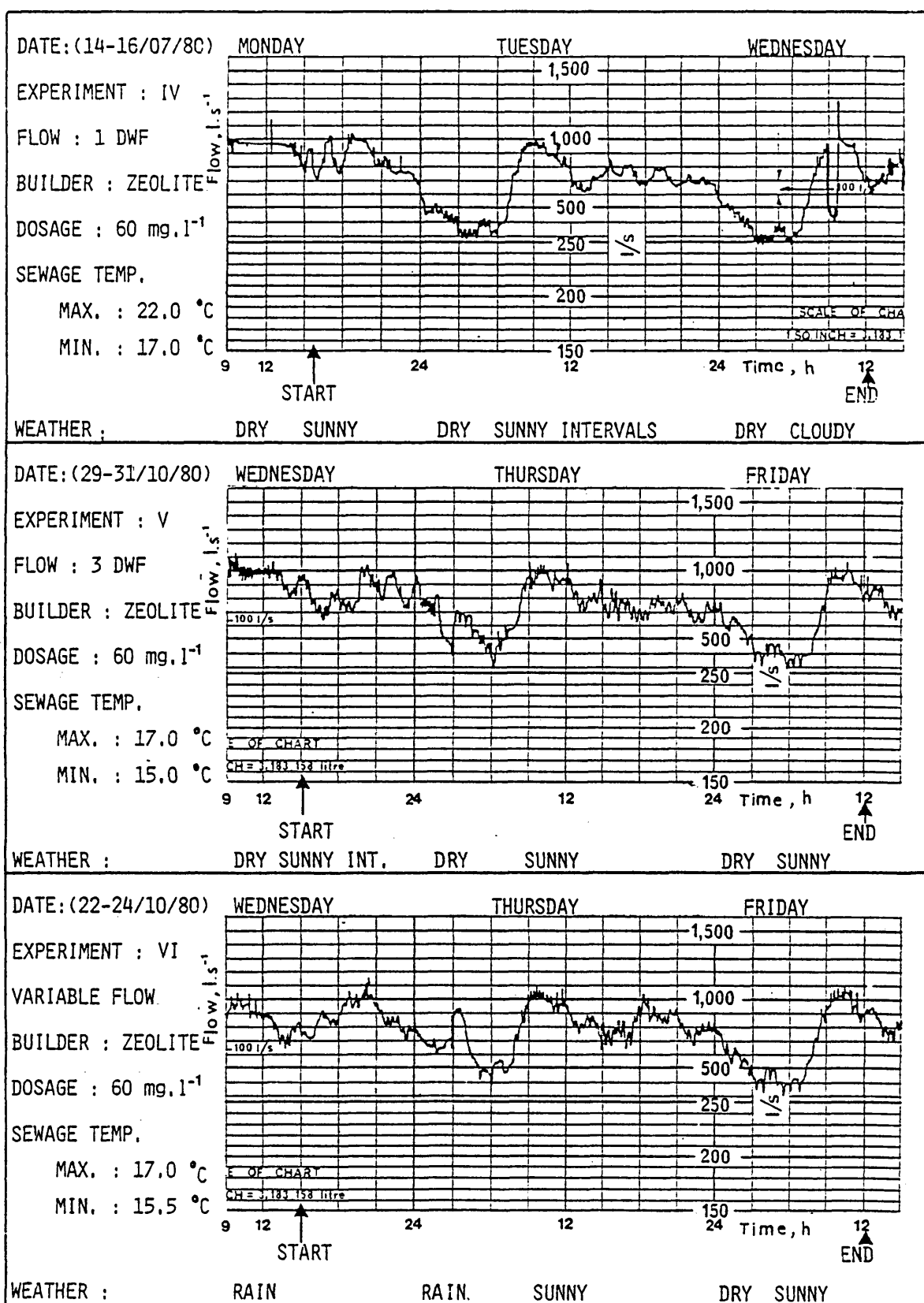


Figure 12 - Flow record from Hogsmill Valley Sewage Treatment Works, maximum and minimum temperature for sewage and weather conditions during experiments at 1 DWF, 3 DWF and Variable flow when zeolite type A was added at 60 mg.l^{-1} .

Table 22 - Influent and effluent suspended solids concentrations, suspended solids removals, influent COD, COD removals, zeolite concentrations effectively added and zeolite removals during primary sedimentation at different flow conditions and different zeolite dosages.

Parameter	System	Zeolite added at 30 mg ℓ^{-1}			Zeolite added at 60 mg ℓ^{-1}		
		1 DWF	3 DWF	Variable Flow	1 DWF	3 DWF	Variable Flow
Influent SS* mg ℓ^{-1}	Control	322	309	155	262	391	190
	Test	351	338	186	319	450	248
Effluent SS* mg ℓ^{-1}	Control	162 †	157	121 †	136 †	134 †	133 †
	Test	185 †	164	144 †	169 †	164 †	167 †
SS Removal %	Control	50	49	22	48	66	30
	Test	47	51	23	47	64	33
Influent COD** mg ℓ^{-1}		495	410	-	362	454	-
COD Removal %	Control	36	41	-	25	43	-
	Test	34	38	-	25	43	-
Zeolite effectively added mg ℓ^{-1}		29	29	31	57	59	58
Zeolite Recovery*** %		112	103	97	91	95	78
Zeolite Removal %		71	66	76	70	66	76

* mean value from samples collected at 3 h intervals.

** value from composite samples

*** zeolite recovery = $\frac{\text{Zeolite determined in influent}}{\text{Zeolite dosed}} \times 100$

† indicates that the means are statistically different at 5% level of significance.

are typical of those in the full scale plant under these conditions, similarly the influent suspended solids during variable flow are more typical of those during a storm condition.

The experiment at 3 DWF and an influent zeolite concentration of $30 \text{ mg } \ell^{-1}$ was undertaken when the flow to the works was normal and thus the influent solids are higher than would be expected if the flow was 3 DWF. When the experiment at 3 DWF with an influent zeolite concentration of $60 \text{ mg } \ell^{-1}$ was undertaken storm water was being returned to the head of the Works resulting in influent suspended solids concentrations more typical of a normal flow to the Works. It is evident that the range of influent conditions encountered in these experiments had little effect on zeolite removal (Table 22). Recoveries of zeolite type A varied between 112 and 78% although the latter figure (one experiment only) is somewhat low, the values are consistent with the accuracy of zeolite type A estimation by aluminium analysis (Carrondo *et al.*, 1979a). Thus the results presented for zeolite removal are not subject to either serious sampling or analytical errors. The removal of zeolite appears to have been unaffected by its influent concentration under all conditions. Removal was consistently lower at 3 DWF (66% in both experiments) than 1 DWF (71 and 70%), although average suspended solids removals were either independent of this trend or exhibited the reverse. Surprisingly zeolite removal was highest under variable flow conditions (76% in both experiments) whilst average suspended solids removals were the worst under these conditions. Removal of zeolite appears to have been little affected under all hydraulic conditions with a range of 66 to 76%. It is evident that at full scale zeolite removal would be equal to or slightly better than average suspended solids removal.

4.5.2 Influence of zeolite type A on heavy metal removal during primary sedimentation

To permit the impact of zeolite on heavy metal removal to be estimated six of the so-called "heavy metals" cadmium, chromium, copper, lead, nickel and zinc were determined in influent and effluent samples collected at 3 h intervals in the preceeding experiments. The results are presented graphically in Figs. 13 to 18. The mean concentration, relative standard deviation and range for the influent, control effluent

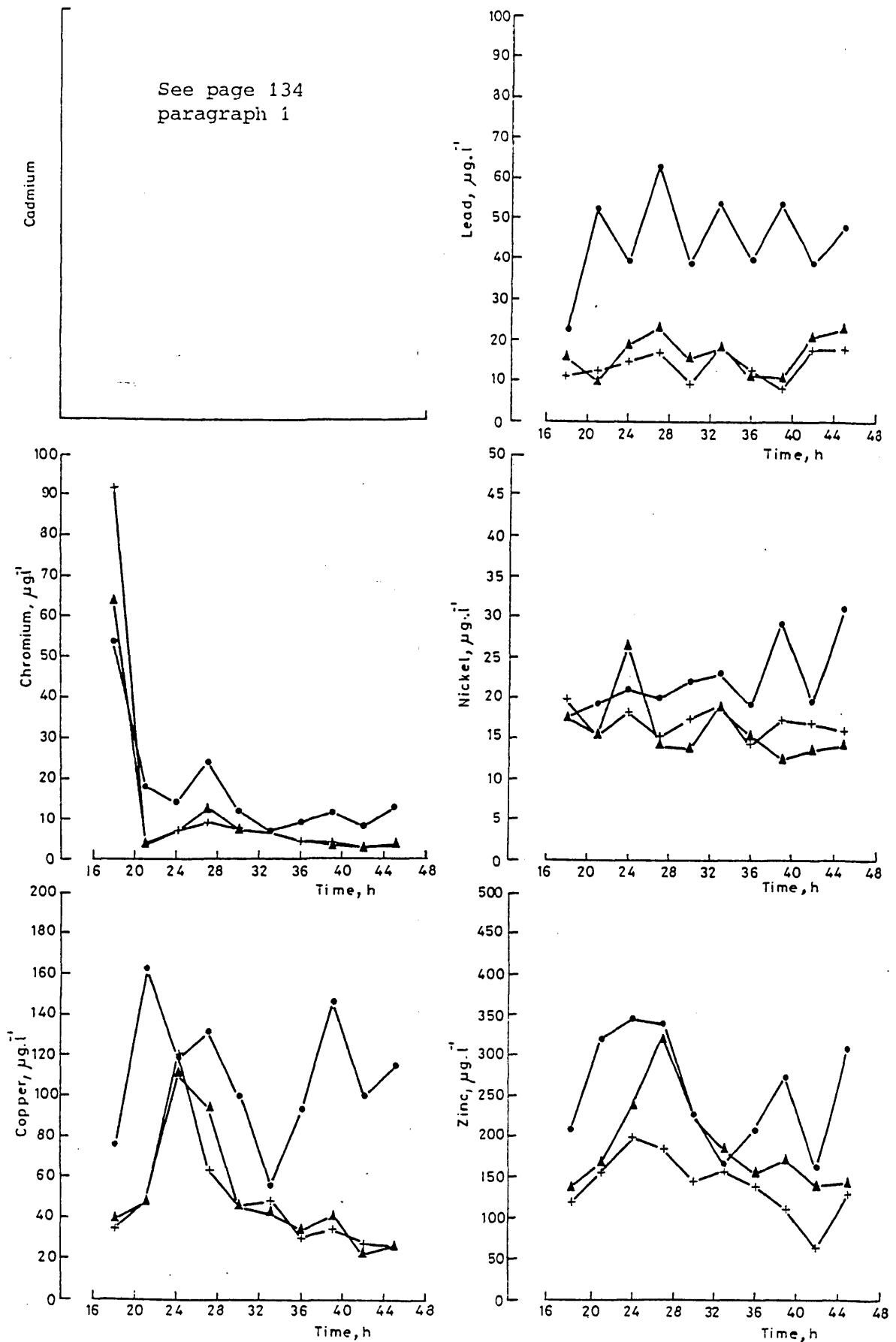


Figure 13 - Variation in heavy metal concentrations in influent (—●—), effluent control (---▲---) and effluent test (---+---) from primary sedimentation pilot plant under 1 DWF condition and when zeolite type A was added at 30 mg l^{-1} .

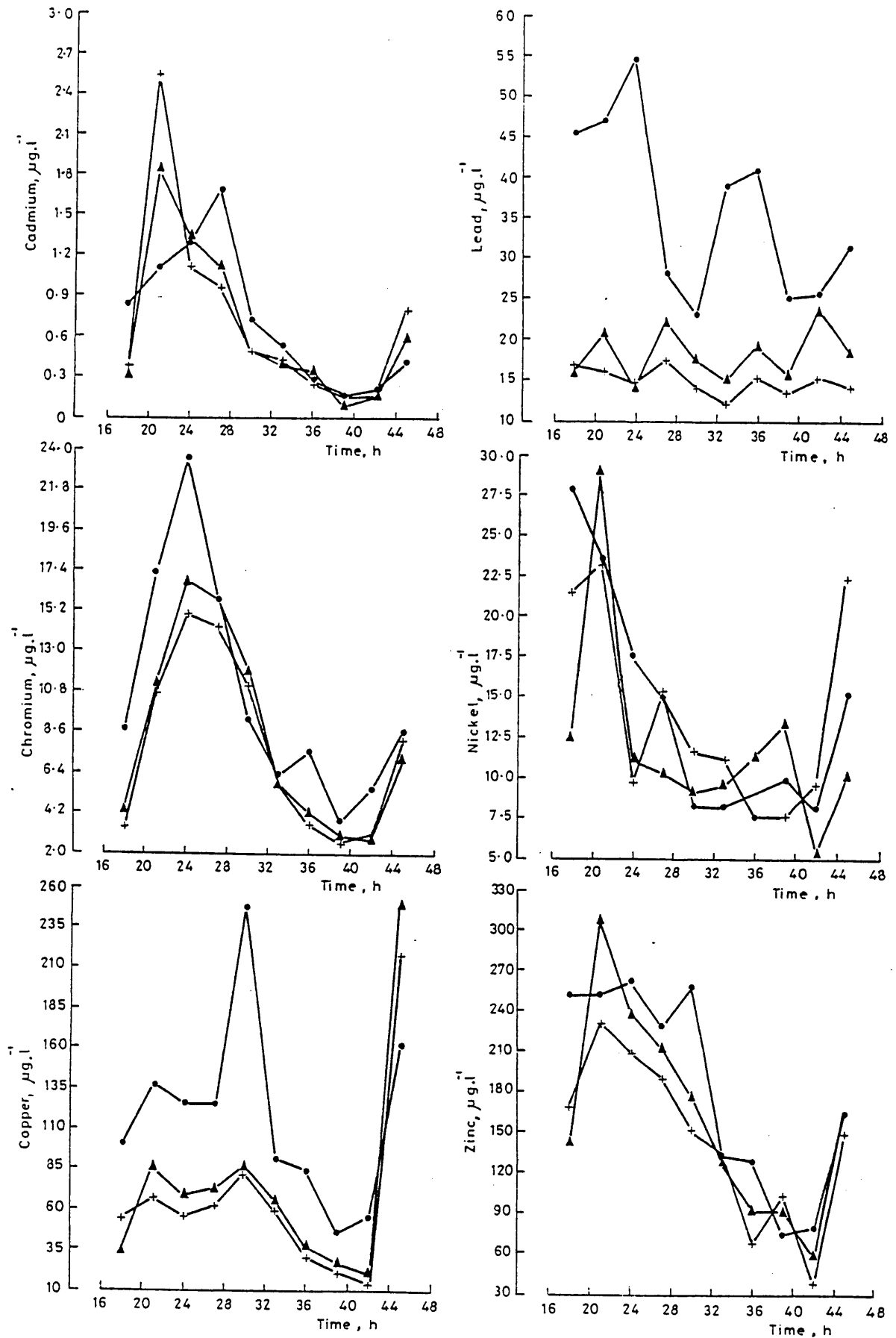


Figure 14 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 3 DWF condition and when zeolite type A was added at 30 mg l^{-1} .

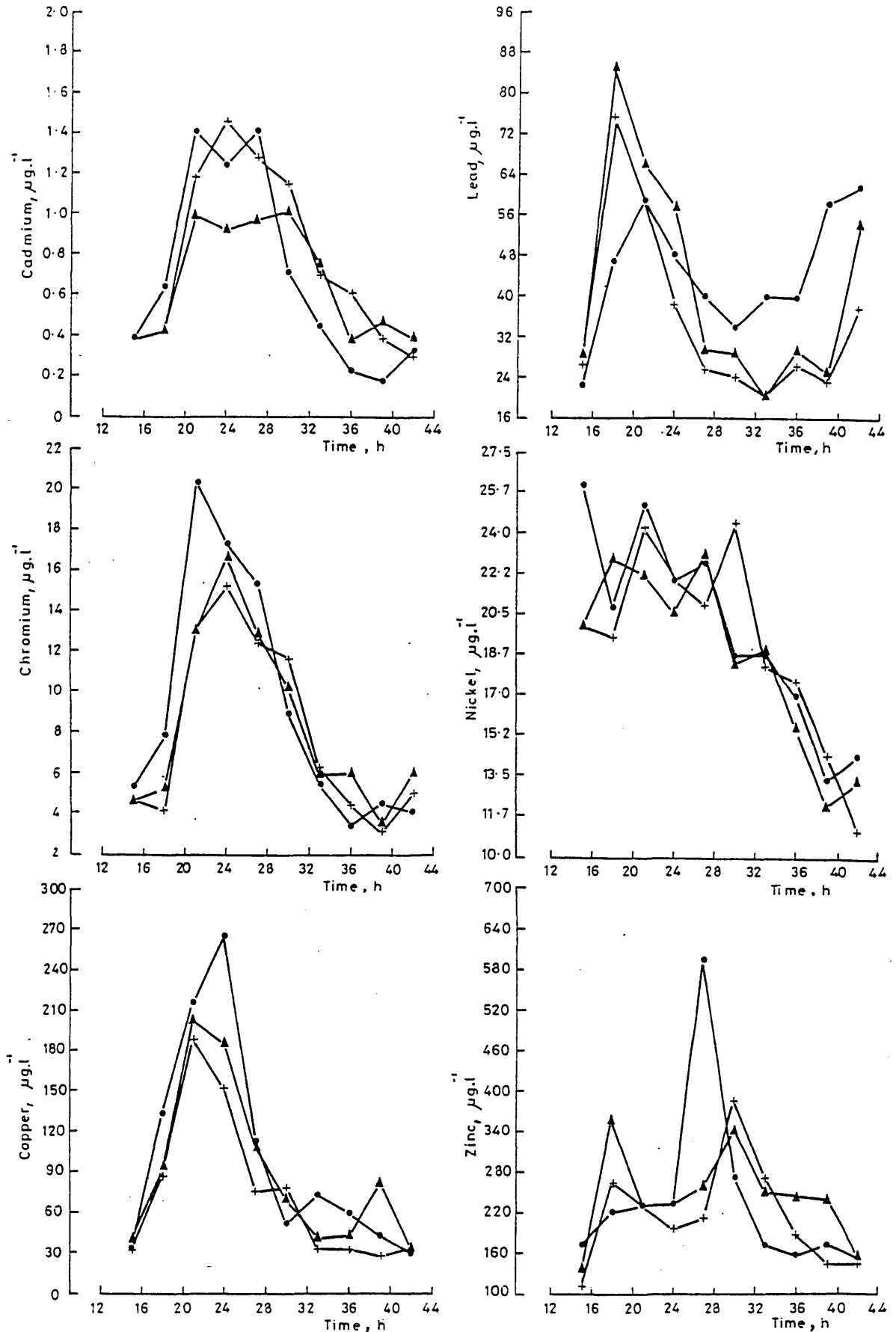


Figure 15 - Variation in heavy metal concentrations in influent (—●—). effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under variable flow condition and when zeolite type A was added at $30 \text{ mg } \ell^{-1}$.

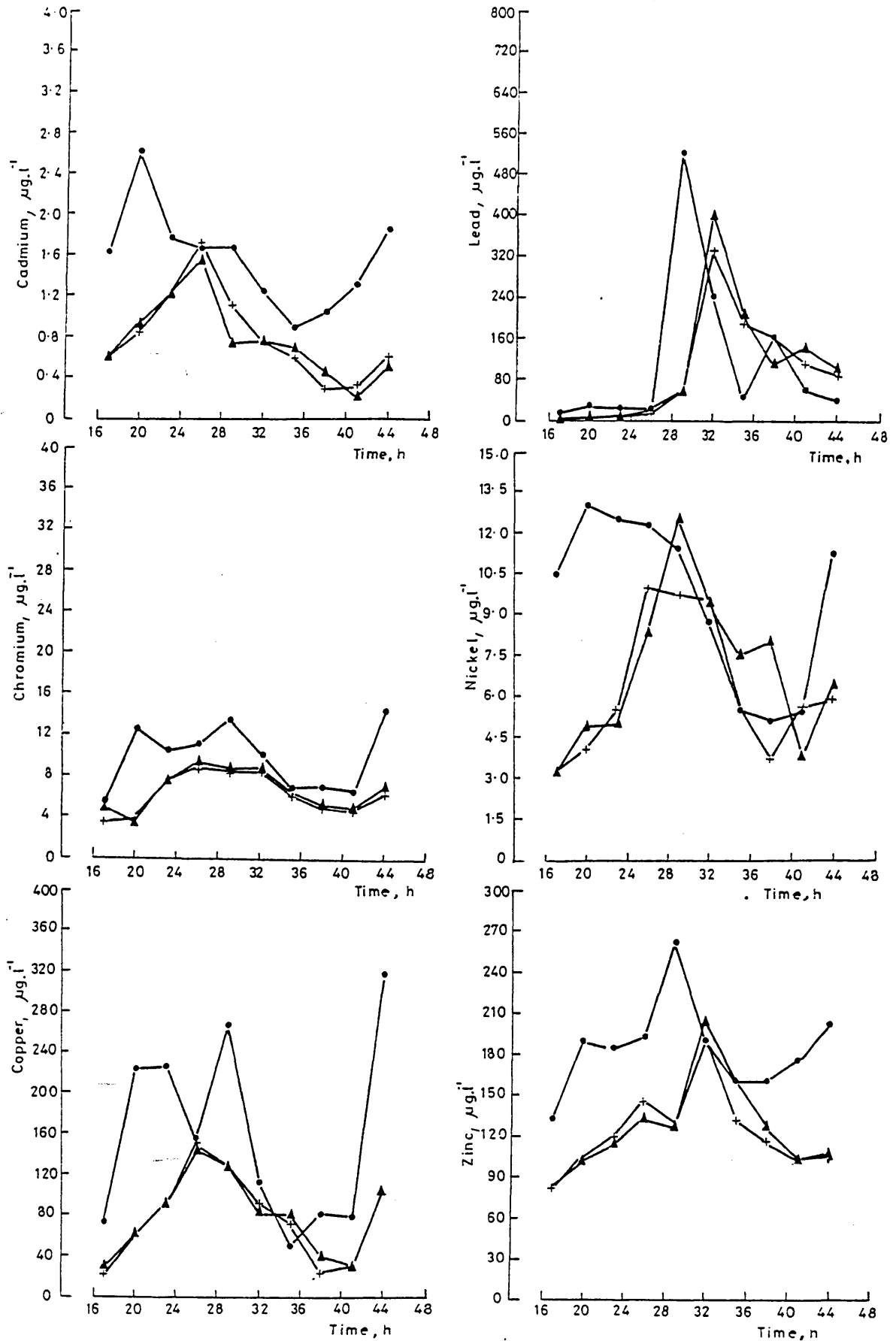


Figure 16 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 1 DWF condition and when zeolite type A was added at 60 mg l^{-1} .

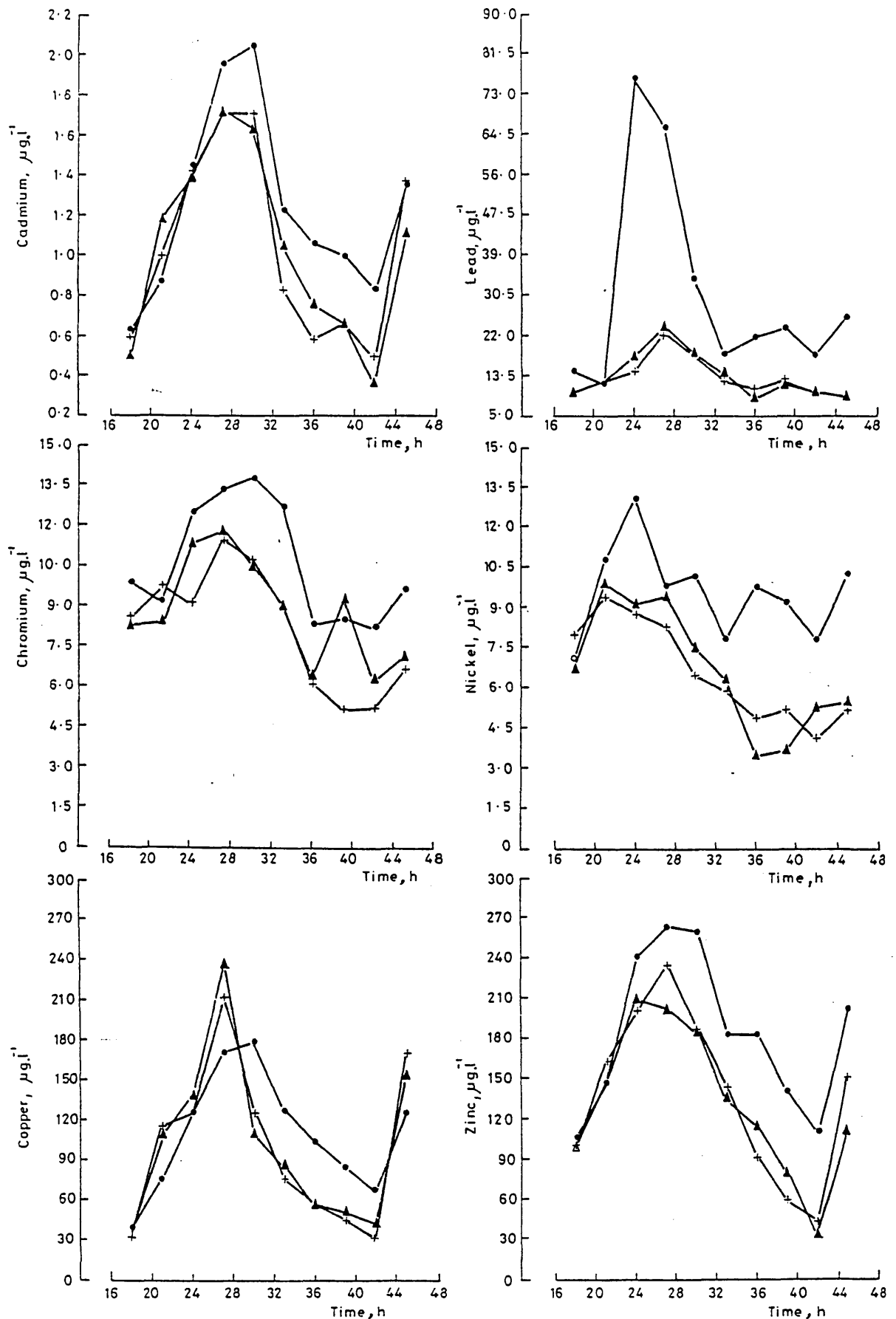


Figure 17 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 3 DWF condition and when zeolite type A was added at $60 \text{ mg } \ell^{-1}$.

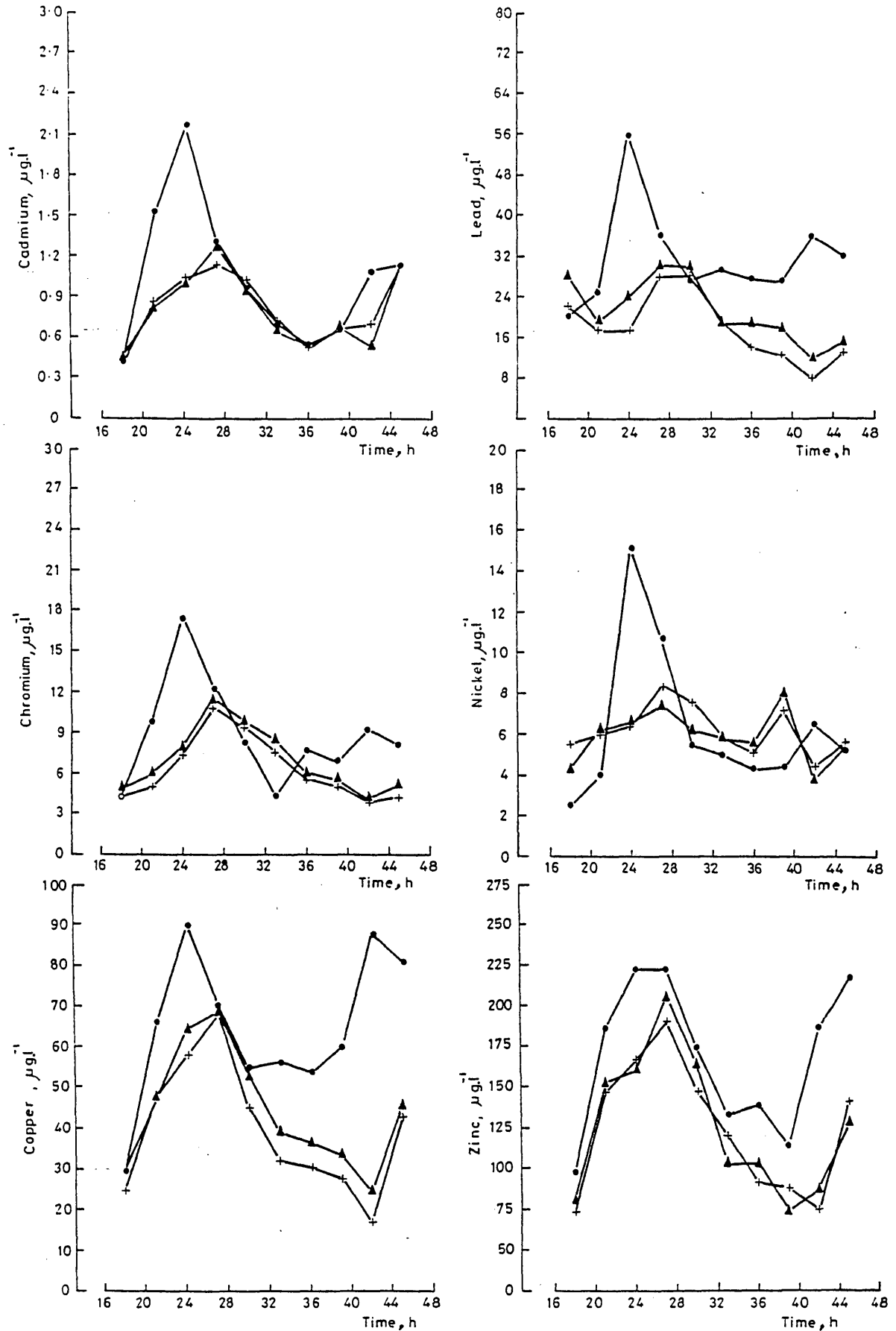


Figure 18 - Variation in heavy metal concentrations in influent ($\bullet$), effluent control ($\blacktriangle$) and effluent test ($+$) from primary sedimentation pilot plant under variable flow condition and when zeolite type A was added at 60 mg l^{-1} .

and test effluent are presented in Table 23. During the experiment at 1 DWF when $30 \text{ mg } \ell^{-1}$ of zeolite was added the concentrations of cadmium in the influent sewage were approximately $0.20 \mu\text{g } \ell^{-1}$. In the effluent the concentrations could not be determined reliably due to the low signal to noise ratios obtained at low concentrations of cadmium. Therefore no data are presented for this metal. Metal concentrations during variable flow were calculated in the same manner as described for suspended solids in section 4.4.2.

From an examination of Fig. 13 it is possible to see an improvement due to the presence of zeolite on lead and zinc removals. Nickel removal appeared to be effected but the pattern of behaviour in Fig. 13 is not consistent. However, from a statistical analysis of the results (section 3.11) presented in Table 23 it can be seen that only lead and zinc concentrations in the effluent control and test plant were statistically different which suggested better removal of these metals in the presence of zeolite.

In the experiment at 3 DWF when zeolite was added at $30 \text{ mg } \ell^{-1}$ (Fig. 14), lead removal was higher in the presence of zeolite. Copper and zinc concentrations were lower in the test effluent during part of the experiment, however considered over the whole period of the experiment no significant differences were found for the removal of these metals in the presence of zeolite.

At variable flow (Fig. 15) it is clear that lead was removed better in the test plant. Zinc and copper removal was improved during part of the experiment but the statistical analysis indicated no significant difference in removals in the presence of $30 \text{ mg } \ell^{-1}$ of zeolite for these two metals.

Chromium removal was improved in the presence of $60 \text{ mg } \ell^{-1}$ of zeolite during 1 DWF simulation (Fig. 16) and its removal was statistically significant. All the other metal removals were not affected significantly by the presence of zeolite. At 3 DWF (Fig. 17) when zeolite was dosed at $60 \text{ mg } \ell^{-1}$, the removal of chromium, lead and nickel seemed to be influenced by the presence of zeolite, however this was not confirmed by the "t" test. Chromium, copper and lead presented better removals in the presence of zeolite at $60 \text{ mg } \ell^{-1}$ during the variable flow simulation (Fig. 18). This observation was confirmed statistically.

Table 23 - Heavy metal concentrations during primary sedimentation when zeolite type A was added at 30 and 60 mg ℓ^{-1}

Metal	System	Zeolite added at 30 mg ℓ^{-1}									Zeolite added at 60 mg ℓ^{-1}								
		1 DWF			3 DWF			Variable Flow			1 DWF			3 DWF			Variable Flow		
		Mean	RSD %	Range	Mean	RSD %	Range	Mean	RSD %	Range	Mean	RSD %	Range	Mean	RSD %	Range	Mean	RSD %	Range
Cadmium	Influent	-	-	-	0.72	66	0.17-1.69	0.70	65	0.18-1.41	1.58	29	0.90-2.62	1.24	36	0.63-2.05	1.05	48	0.55-2.18
	Effluent Control	-	-	-	0.66	82	0.09-1.84	0.70	38	0.38-1.01	0.87	50	0.22-1.62	1.03	43	0.36-1.72	0.80	33	0.45-1.27
	Effluent Test	-	-	-	0.73	94	0.15-2.54	0.83	50	0.30-1.46	0.81	51	0.30-1.72	1.09	44	0.49-1.71	0.82	30	0.40-1.14
Chromium	Influent	16.8	78	8.8-53.6	10.7	55	3.8-23.5	9.2	63	3.4-20.3	9.9	30	5.6-14.6	10.6	20	8.2-13.8	8.8	41	4.3- 17.4
	Effluent Control	11.3	156	2.6-63.4	8.3	60	2.8-16.8	8.4	50	3.5-16.6	6.7*	28	3.4-9.4	8.8	21	6.3-11.8	7.0*	33	4.2- 11.5
	Effluent Test	13.9	187	2.8-91.7	7.8	58	3.1-15.0	8.0	54	3.1-15.2	6.3*	30	3.6-8.8	8.2	26	5.2-11.5	6.3*	36	4.3- 10.9
Copper	Influent	110	28	56-163	118	47	47-248	102	75	30-265	158	56	79-316	110	39	39-179	65	27	30-90
	Effluent Control	51	54	23-111	75	83	21-250	84	72	23-202	79	47	30-144	102	58	38-237	44*	31	25-69
	Effluent Test	49	55	28-121	67	82	15-220	74	72	28-188	77	54	22-149	99	59	32-212	39*	38	17-68
Lead	Influent	45	24	22-63	36	29	23-55	45	26	34-59	117	130	14-525	31	68	12-77	32	29	20-56
	Effluent Control	17*	28	10-23	18*	17	14-24	43*	48	21-85	106	111	5-401	14	35	9-24	21*	29	12-30
	Effluent Test	14*	26	8-18	15*	10	12-17	36*	47	21-75	98	104	5-335	12	37	5-22	18*	35	8-26
Nickel	Influent	22	19	18-30	15	44	8-28	20	20	13-26	10	31	5-13	10	17	8-13	6.3	57	2.5-15.2
	Effluent Control	16	24	12-26	12	49	5-29	19	20	12-23	7	39	3-13	7	32	4-10	5.9	21	3.8- 8.1
	Effluent Test	17	10	14-20	14	42	7-23	19	21	11-25	6	39	3-10	7	27	4-9	6.2	19	4.4- 8.4
Zinc	Influent	256	26	161-345	184	40	75-262	237	53	150-595	185	17	133-262	184	30	110-264	170	26	98-223
	Effluent Control	188*	30	136-321	161	45	59-308	222	29	119-341	127	26	83-205	131	41	33-202	126	33	74-206
	Effluent Test	140*	26	62-199	145	40	68-232	214	35	111-385	123	23	81-191	136	43	44-235	124	31	74-191

* - Indicates that the mean values are different at 5% level of significance.
all values are in $\mu\text{g } \ell^{-1}$

It was evident during this series of experiments that the pattern for metal concentration in the effluent in the presence of zeolite followed the pattern for metal concentration in the effluent from the control plant. In the cases of improved metal removal the test pattern was parallel to the control but lower. This suggests that the effect of zeolite type A is more due to its ion exchange capacity than any effect as a flocculant aid which could also enhance the metal removal during the sedimentation.

It is evident from Table 23 that influent concentrations of chromium, lead and nickel were an order of magnitude higher than those of cadmium. Whilst the influent concentrations of copper and zinc were an additional order of magnitude greater than those of chromium, nickel and lead, zinc exhibiting the highest influent concentration of all the metals determined. During the six experiments the variation in mean influent concentration was least for zinc being approximately 50% whilst chromium and copper varied by about 80%, the variation in mean influent cadmium, lead and nickel concentrations were between three and four fold. In general lower influent concentrations of most heavy metals were encountered during the experiments at variable flow when the flow to the Works was elevated than during the experiments at 1 DWF when the flow to the Works was normal. Despite the nature of the flow to the Works being different during the experiments at 3 DWF the influent heavy metals concentrations appear to be comparable.

Metal removal has been calculated by two methods, method 1 based on the average values for influent and effluent concentrations determined from the 3 h samples and method 2 using the concentrations retained by the sludge solids in the tank and the concentrations in the influent composite sample collected during all three days of the experiment. Mass balances were also calculated for each metal during the six experiments, these are also included in Table 24. Methods of calculating removal and mass balances are presented in Appendix IV. It was not possible to generate a composite sample during the variable flow experiment and therefore a mass balance could not be calculated. The mass balances for chromium, copper, nickel and zinc are reasonably good for all experiments. Those of cadmium and lead include some which are rather poor, this reflects the nature of cadmium and lead discharges and the frequency of sampling. It is evident that for all the heavy

Table 24 - Percentage removal and mass balance for heavy metals during primary sedimentation at different flow conditions when zeolite was added at 30 and 60 mg ℓ^{-1}

Metal	Parameter	Zeolite added at 30 mg ℓ^{-1}						Zeolite added at 60 mg ℓ^{-1}					
		1 DWF		3 DWF		Variable Flow		1 DWF		3 DWF		Variable Flow	
		Control	Test	Control	Test	Control	Test	Control	Test	Control	Test	Control	Test
Cadmium	% Removal 1	-	-	8	0	5	(-) 5	45	48	17	13	26	26
	% Removal 2	-	-	14	15	-	-	35	40	29	32	-	-
	Mass Balance	-	-	176	154	-	-	140	120	102	99	-	-
Chromium	% Removal 1	33	17	22	27	12	17	32*	35*	17	23	24*	31*
	% Removal 2	17	19	67	66	-	-	51	69	59	70	-	-
	Mass Balance	104	98	71	72	-	-	89	74	82	72	-	-
Copper	% Removal 1	54	56	58	62	19	28	50	51	7	10	33*	40*
	% Removal 2	80	84	86	86	-	-	39	51	44	52	-	-
	Mass Balance	81	85	74	75	-	-	104	91	89	84	-	-
Lead	% Removal 1	63*	72*	50*	59*	4*	18*	10	17	57	60	34*	44*
	% Removal 2	102	109	174	217	-	-	63	107	55	60	-	-
	Mass Balance	67	73	42	37	-	-	65	51	108	102	-	-
Nickel	% Removal 1	27	24	18	5	5	3	28	34	30	31	14	10
	% Removal 2	43	53	8	11	-	-	34	40	26	24	-	-
	Mass Balance	77	72	108	115	-	-	97	99	125	104	-	-
Zinc	% Removal 1	27*	45*	12	18	7	10	32	34	29	25	26	27
	% Removal 2	48	54	40	48	-	-	45	46	34	38	-	-
	Mass Balance	73	72	78	81	-	-	104	95	118	104	-	-

(-) Indicates metal mobilization.

* Indicates that the effluent concentrations for control and test are different at 5% level of significance.

metals both in control and test plant the highest removals were achieved when calculated on the basis of metal retained in the sludge solids (method 2). Unfortunately, it is not possible to undertake statistical analysis of the removals calculated in this manner since necessarily they are calculated for a single value for heavy metal concentrations in the sludge because only one sample was produced per experiment. However, removals calculated by method 1 using pairs of values which were statistically analysed using the Student "t" test (Table 23) for chromium, copper, lead and zinc were statistically different.

Metals were analysed in samples from the sludge solids in the tanks at the end of the experiments, these results are presented in Table 25. They clearly indicate that the lower the metal concentration in the effluent the higher the metal concentration in the sludge for the four metals mentioned previously. Chromium concentration in the sludge solids during variable flow experiments, when zeolite was added at $60 \text{ mg } \ell^{-1}$, was higher in the control which was not expected since removal for chromium in the control was higher than in the test (Table 24). However the difference was so small that it does not compromise the previous statement.

The influence of zeolite on metal removal appeared to be little influenced by hydraulic loading and influent zeolite concentration. Although with an influent zeolite concentration of $60 \text{ mg } \ell^{-1}$ three of the four significant effects observed were at variable flow. The highest percentage improvement observed in metal removal was that of zinc although it was only significantly affected once at 1 DWF with an influent zeolite type A concentration of $30 \text{ mg } \ell^{-1}$ when an 18% improvement was recorded. The lowest significant improvement was that of chromium at 1 DWF and $60 \text{ mg } \ell^{-1}$ of zeolite in the influent which increased removal by 4%. Removal of copper was significantly affected only once at variable flow with an influent zeolite concentration of $60 \text{ mg } \ell^{-1}$ where a 7% improvement occurred. The improvement in the removal of lead was the most frequently observed where increases of between 9 and 4% were observed in 4 of the six experiments.

Table 25 - Heavy metal concentrations in sludge solids from the experiments using zeolite type A at 30 and 60 mg ℓ^{-1} and different flow conditions

Metal	Zeolite added at 30 mg ℓ^{-1}						Zeolite added at 60 mg ℓ^{-1}					
	1 DWF		3 DWF		Variable Flow		1 DWF		3 DWF		Variable Flow	
	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test	Control Test
Cadmium	-	-	8.9	9.8	9.5	9.6	10.7	11.5	41.0	44.9	13.8	17.5
Chromium	136	144	372	362	131	134	97.6*	134.4*	490	575	117*	112*
Copper	2106	2118	5460	5523	469	509	1179	1554	3944	4538	929*	982*
Lead	962*	994*	2891*	3677*	1141*	1147*	943	1621	1359	1479	948*	1133*
Nickel	182	217	79.2	101.7	72.9	96.6	64.9	77.9	203	261	63.1	80.1
Zinc	2392*	2597*	5261	6455	1840	1817	1527	1901	5006	5542	1707	2064

all concentrations are in $\mu\text{g } \ell^{-1}$

* Means that a statistically significant difference between metal concentration in the effluents was detected at 5% level of significance

4.6 Behaviour of NTA during primary sedimentation at different hydraulic loadings and influent NTA concentrations.

4.6.1 The removal of NTA during primary sedimentation

Six experiments were undertaken to assess the removal of NTA during primary sedimentation. Two influent concentrations of NTA were selected 15 and 30 mg ℓ^{-1} and three different flow conditions, i.e. 1 DWF, 3 DWF and variable flow. The experiments under variable flow conditions were designed to simulate the diurnal variation of condensed phosphate concentration in raw sewage. During previous experiments a peak in the polyphosphate concentration occurred at approximately midnight (see Fig. 43 Appendix V). At this time the flow was normally lower, consequently the retention time in the tanks was higher. Thus any increase in NTA concentration during this period would have a greater contact time during which metals could be mobilized from the settling sludge. To simulate this situation NTA was dosed at variable rates to achieve a peak concentration at 23:00 or 24:00 h while the flow was varied using the cam. The flow pattern used is shown in Fig. 19 and the pattern of the variation in NTA concentration is shown in Fig. 20.

The weather conditions were recorded during the experiments and are presented in Fig. 21 and 22. In the same figures the influent flow recorded from the Works and the sewage temperature (maximum and minimum) are presented.

During the experiments influent and effluent suspended solids were determined and the percentage removals were calculated by method 1 (see Appendix IV), the results are presented in Table 26. Suspended solids during variable flow were calculated in the same manner as described in section 4.4.2. The weather was mainly dry during the 1 DWF experiments except at the end of the period when NTA was added at 30 mg ℓ^{-1} . Despite this the influent suspended solids during the 1 DWF experiments were in the same range, the difference in removals are probably explained by the different characteristics of the influent sewage.

During the experiments at 3 DWF the weather was dry, there was some rain before the start of both experiments and high values for influent solids were registered.

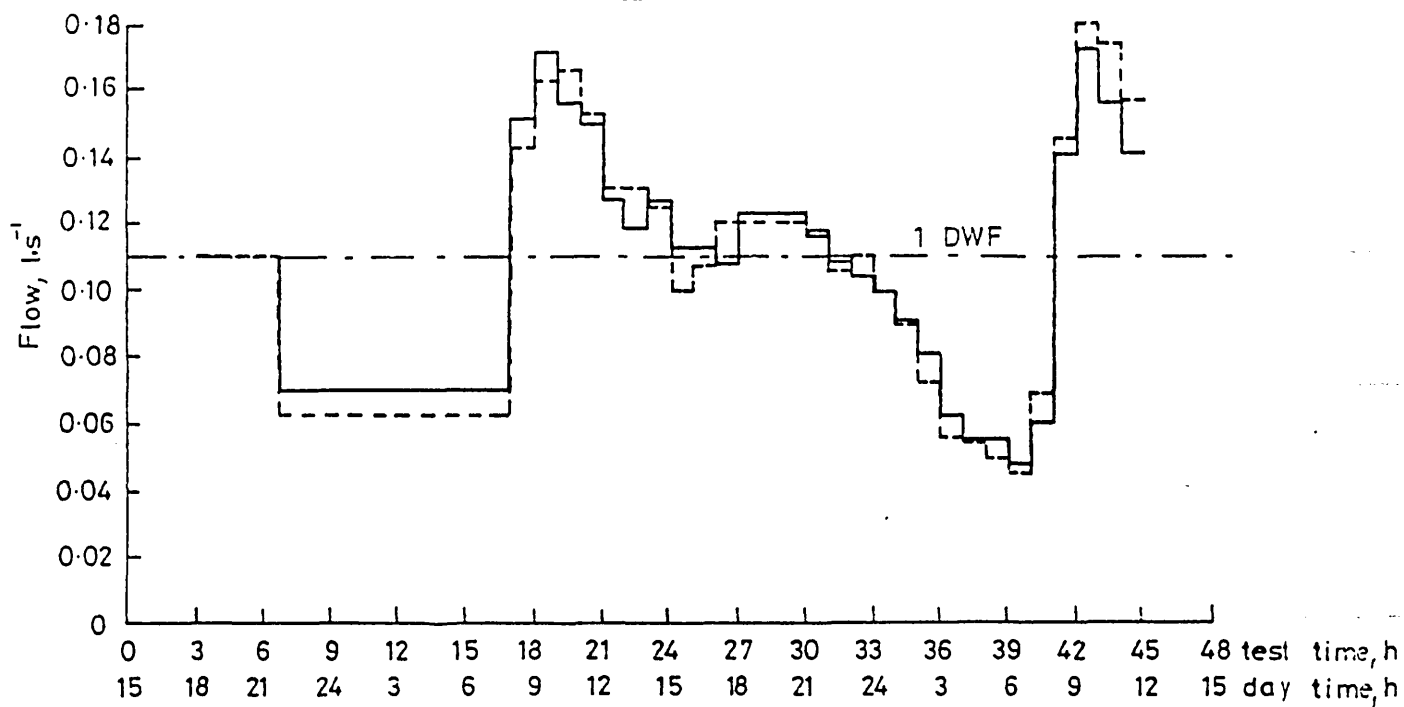


Figure 19 - Flow during NTA experiments under variable flow conditions
 (—NTA concentration 6-34 mg l^{-1} ; --- NTA concentration 10-66 mg l^{-1})

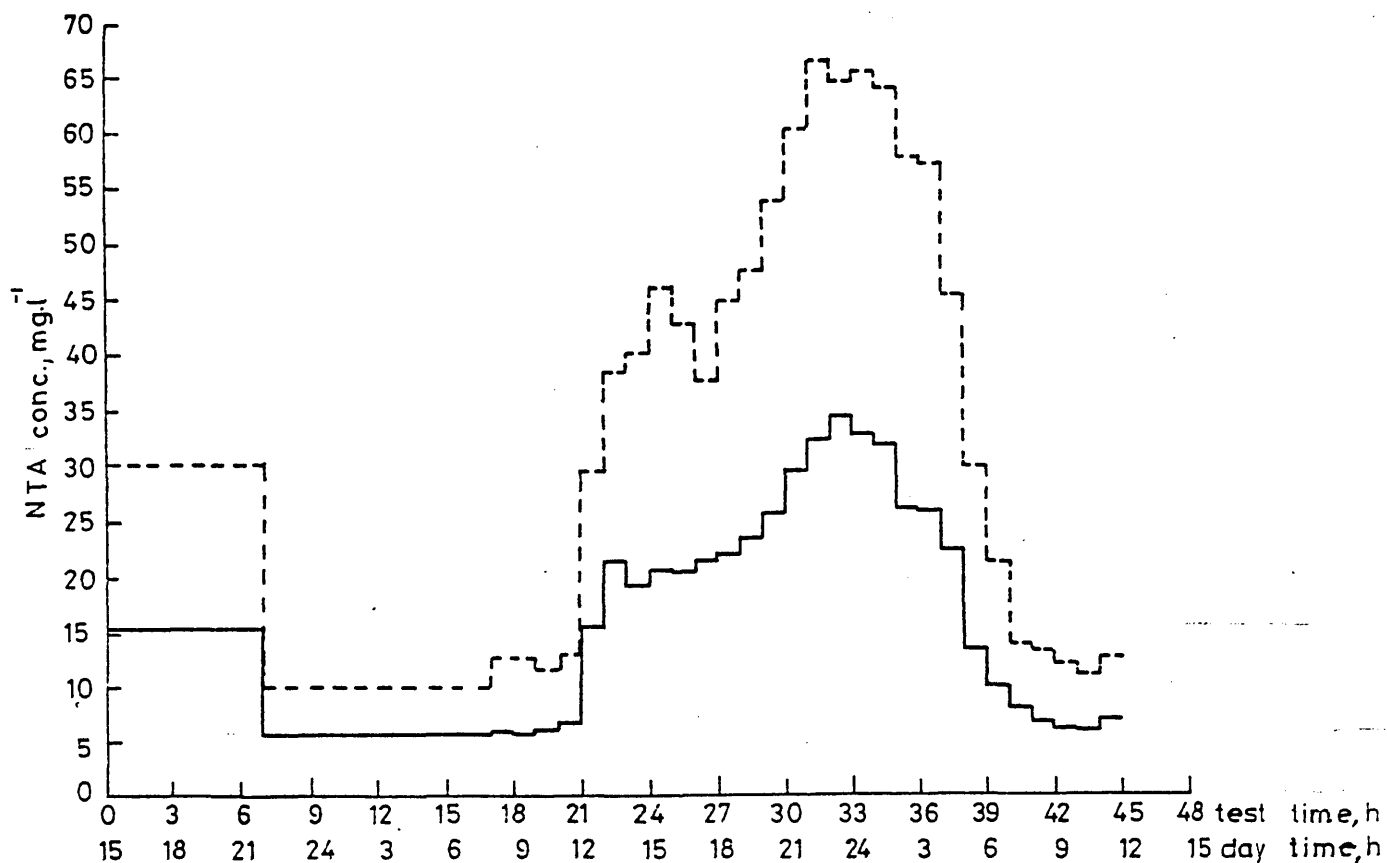


Figure 20 - NTA dosed in different experiments under variable flow conditions (—NTA concentration 6-34 mg l^{-1} ; ---NTA concentration 10-66 mg l^{-1})

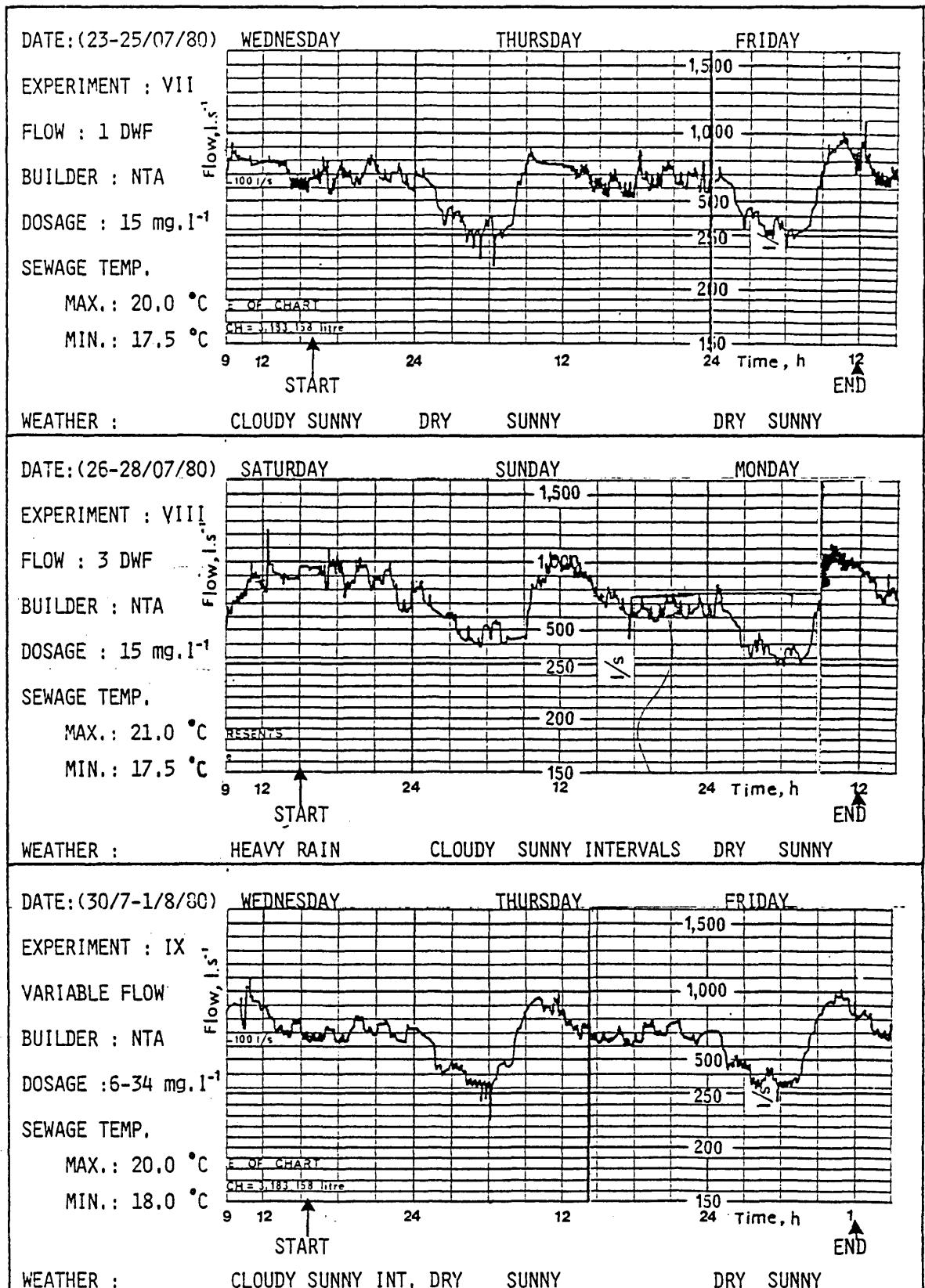


Figure 21 - Flow record from Hogsmill Valley Sewage Treatment Works, maximum and minimum temperature for sewage and weather conditions during experiments at 1 DWF, 3 DWF and Variable flow when NTA was added at 15 mg l⁻¹.

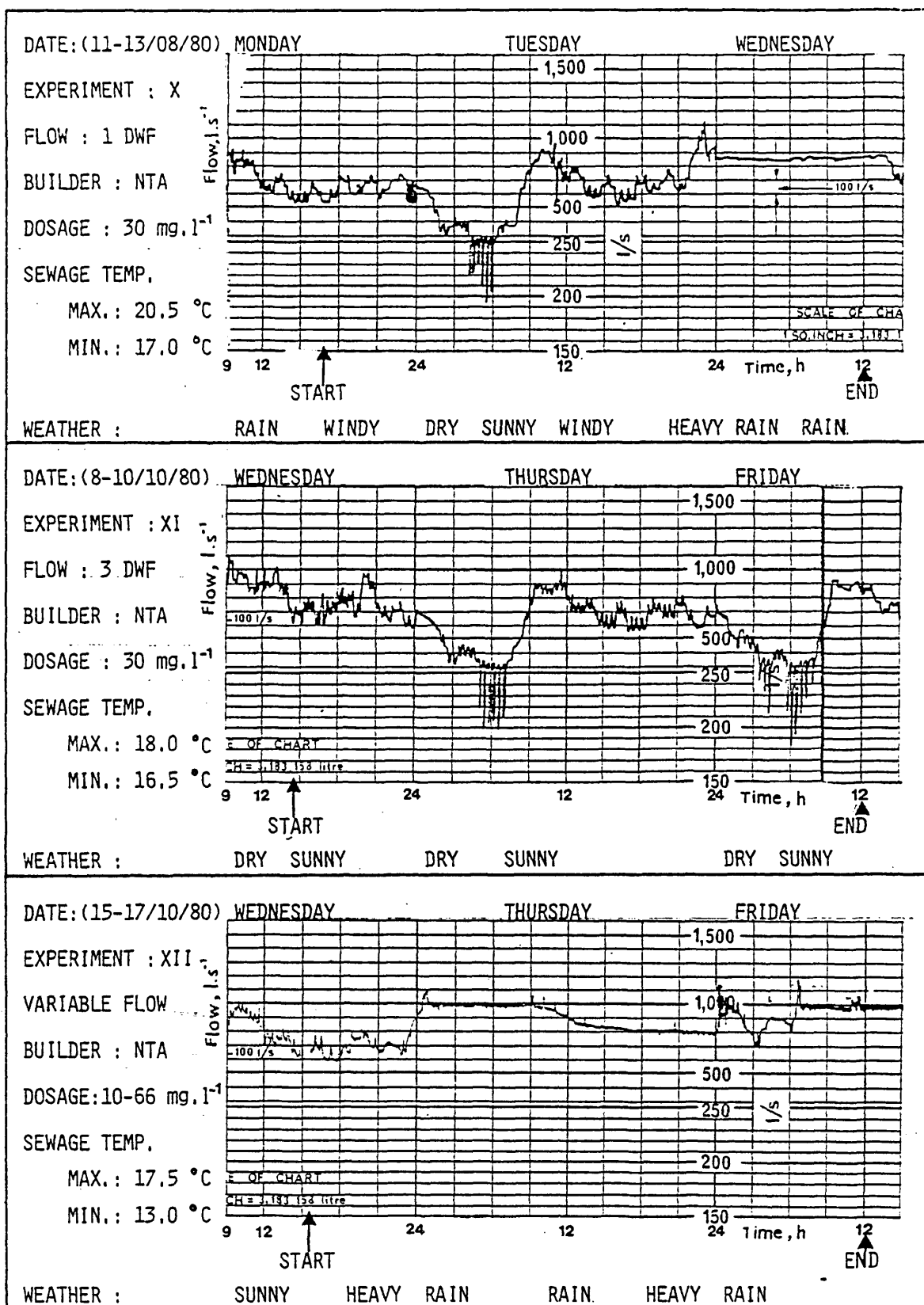


Figure 22 - Flow record from Hogsmill Valley Sewage Treatment Works, maximum and minimum temperature for sewage and weather conditions during experiments at 1 DWF, 3 DWF and Variable flow when NTA was added at 30 mg l^{-1} .

At variable flow conditions dry weather prevailed for the experiment when NTA was added at an average concentration of $15 \text{ mg } \ell^{-1}$, but when the average NTA dosage was increased to $30 \text{ mg } \ell^{-1}$ heavy rain occurred and the sewage was very dilute resulting in very low values for influent suspended solids.

The same correlation between influent suspended solids and percentage removal was observed as in the experiments with zeolite, that is a high suspended solids influent resulted in high percentage removal. The only deviation was observed at variable flow when NTA was added at an average concentration of $30 \text{ mg } \ell^{-1}$ when low influent suspended solids resulted in high percentage removal, which can be explained by the very diluted sewage treated during this experiment having different characteristics than the normal sewage. As can be seen in Table 26 the percentage suspended solids removal in the control and test plants were different and in some experiments these differences were statistically significant. However there was no correlation between suspended solids removal and the presence of NTA. When NTA was added at $15 \text{ mg } \ell^{-1}$ at 1 DWF the removal was higher in its presence whilst at the same concentration but at variable flow it was lower. At 3 DWF with an influent concentration of $30 \text{ mg } \ell^{-1}$ the percentage suspended solids removal in the test was again higher.

Removal of COD, as can be seen in Table 26, was higher in experiments with high influent COD and the COD influent correlated well with suspended solids in the influent. Removal of COD varied from 20 to 50%. However no correlation was observed between the presence of NTA and COD removal.

Concentrations of NTA added during the experiments were calculated from the volume left in the aspirator and the initial volume (section 3.8.1.2) and the average flow through the plant, these are presented in Table 26. The effluent NTA concentrations were obtained by analysis of the 3 h samples and the mean value calculated. For variable flow experiments the mean value for NTA in the effluent was calculated by the same manner as described for the calculation of suspended solids in section 4.4.2. Removals varied from 16 to 40% and these correlated

Table 26 - Influent and effluent suspended solids concentrations, suspended solid removals, influent COD, COD removals, NTA concentration effectively added and NTA removals during primary sedimentation at different flow conditions and different NTA dosages.

Parameter	System	NTA added at 15 mg ℓ^{-1}			NTA added at 30 mg ℓ^{-1}		
		1 DWF	3 DWF	Variable Flow	1 DWF	3 DWF	Variable Flow
Influent SS* mg ℓ^{-1}		274	393	224	251	458	146
Effluent SS mg ℓ^{-1}	control	172†	162	125†	131†	164	72
	test	162	160	143	105	174	67
SS Removal %	control	37	59	44	48	64	51
	test	41	59	36	58	62	54
Influent COD** mg ℓ^{-1}		374	471	-	370	646	-
COD Removal %	control	22	48	-	43	49	-
	test	21	51	-	50	41	-
NTA effectively added mg ℓ^{-1}		15.5	17.0	18.5	33.5	34.5	37.5
NTA removal %		26	24	16	40	18	29

* Based on 3 h sampling

** Based on composite samples

† indicates that the effluent concentration mean values for control and test are different at 5% level of significance.

with the hydraulic conditions. A reduction in retention time reduced NTA removal, which suggests that NTA was removed by adsorption onto the particles and like any other adsorption phenomenon was time dependent. As NTA was determined in filtered effluent samples no account was taken of NTA adsorbed on the effluent suspended solids; from previous experiments an increase of 10% in the effluent NTA concentration would be expected in the presence of typical effluent suspended solids concentrations. This percentage error was constant for all the experiments except during variable flow when NTA was added at an average concentration of $30 \text{ mg } \ell^{-1}$. In this case less than 10% would be more appropriate since the amount of suspended solids in the effluent was very low when compared with the other experiments.

During both experiments at 1 DWF the sewage had similar values for both the suspended solids and COD, it would appear therefore an increase in NTA dosage resulted in an increase in its removal. The above observations confirm that NTA was removed from sewage by adsorption onto insoluble particles which were removed during primary sedimentation.

4.6.2 Influence of NTA on heavy metal removal during primary sedimentation

To assess the effect of NTA on the removal of cadmium, chromium, copper, lead, nickel and zinc, samples from influent and effluent collected at 3 h intervals in the preceeding experiments were analysed for their metallic content. The results were plotted and are presented in Figs. 23 to 28. In Table 27 mean values, relative standard deviations and ranges for influent and effluent metal concentrations are presented.

In the experiment when NTA was added at $15 \text{ mg } \ell^{-1}$ during 1 DWF (Fig. 23) it appears that cadmium, lead, nickel and zinc were mobilized in the effluent in the presence of NTA. This was confirmed by the statistical analysis (section 3.11) which indicates that effluent concentrations of lead, nickel and zinc presented significant differences, with higher values for effluent tests.

At 3 DWF when NTA was added at $15 \text{ mg } \ell^{-1}$ (Fig. 24), lead concentrations were consistently higher in the test effluent. In the majority of samples, zinc exhibited higher values for the effluent test, however

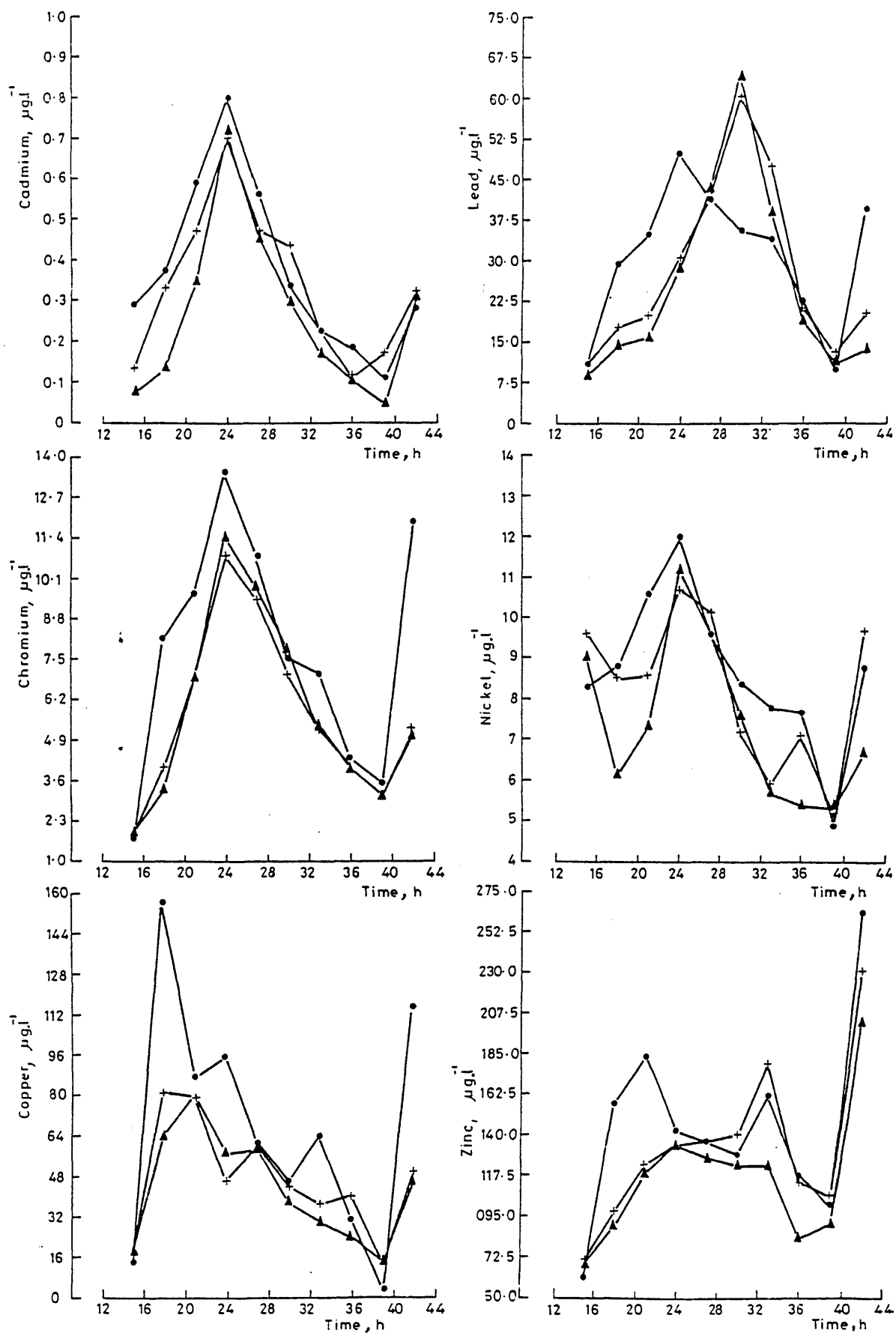


Figure 23 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 1 DWF condition and NTA added at 15 mg l^{-1} .

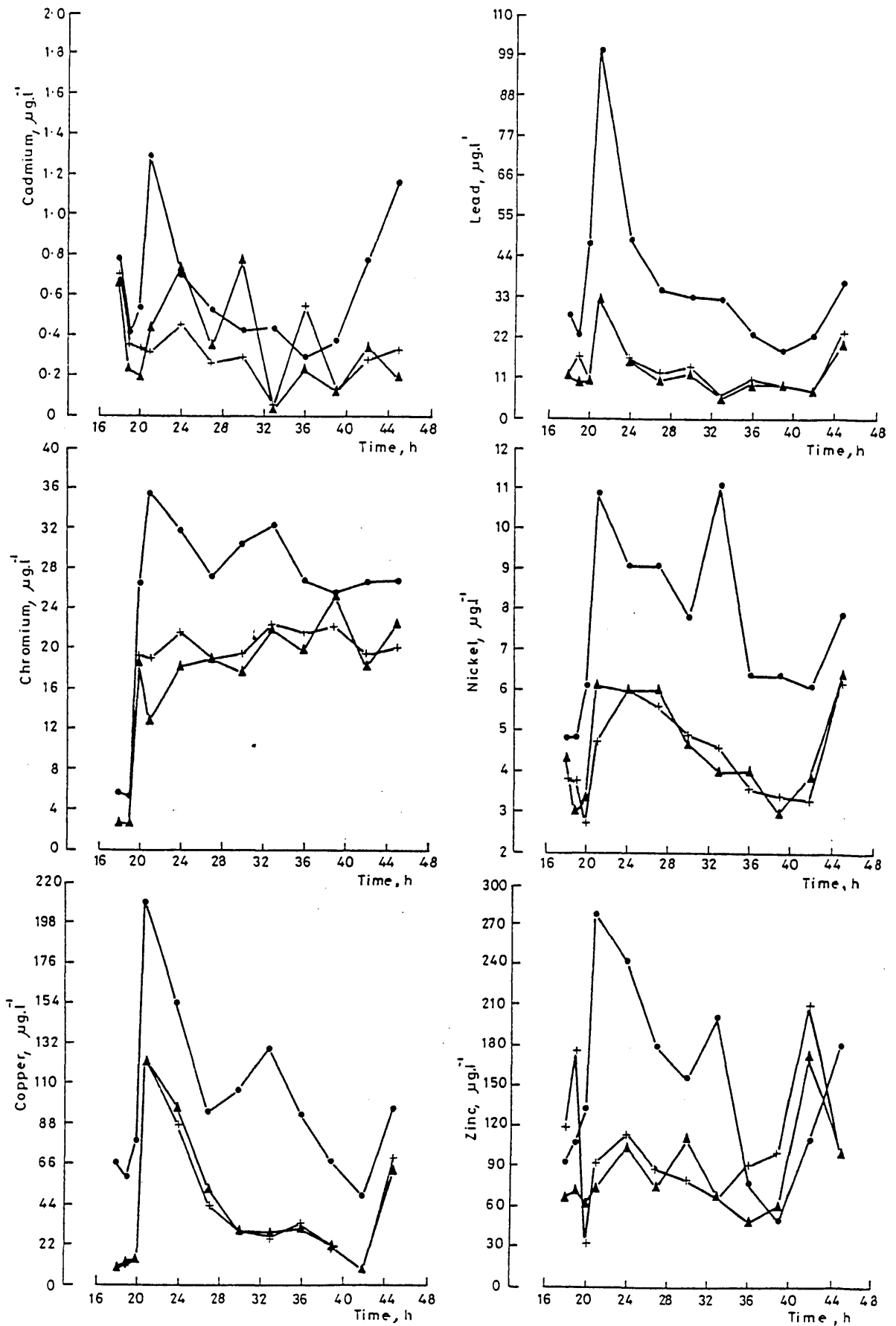


Figure 24 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 3 DWF condition and NTA added at 15 mg l^{-1} .

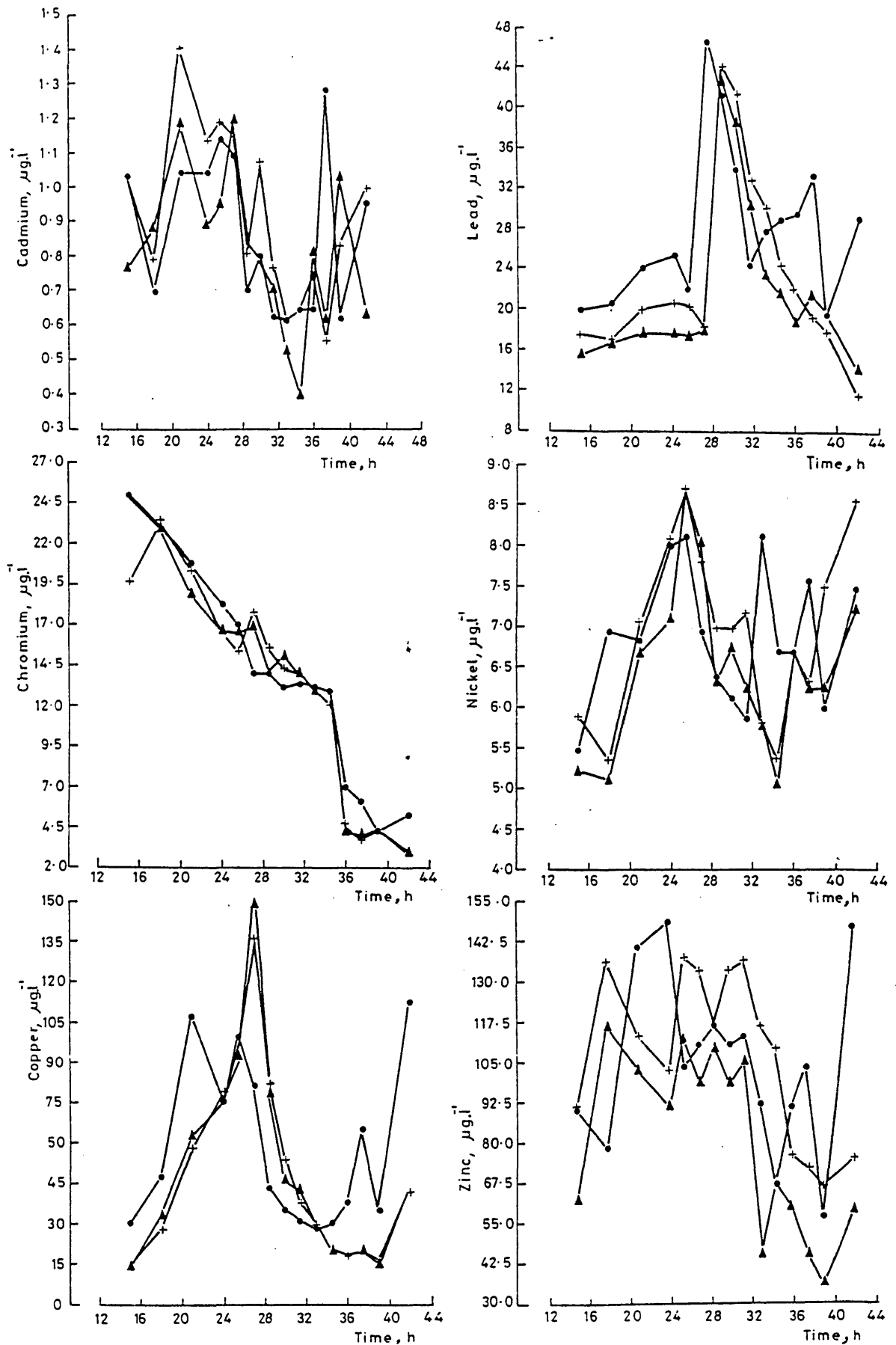


Figure 25 - Variation in heavy metal concentrations in influent ($\bullet$), effluent control ($\blacktriangle$) and effluent test ($+$) from primary sedimentation pilot plant under variable flow condition and NTA added at variable concentrations ($6 - 34 \text{ mg l}^{-1}$).

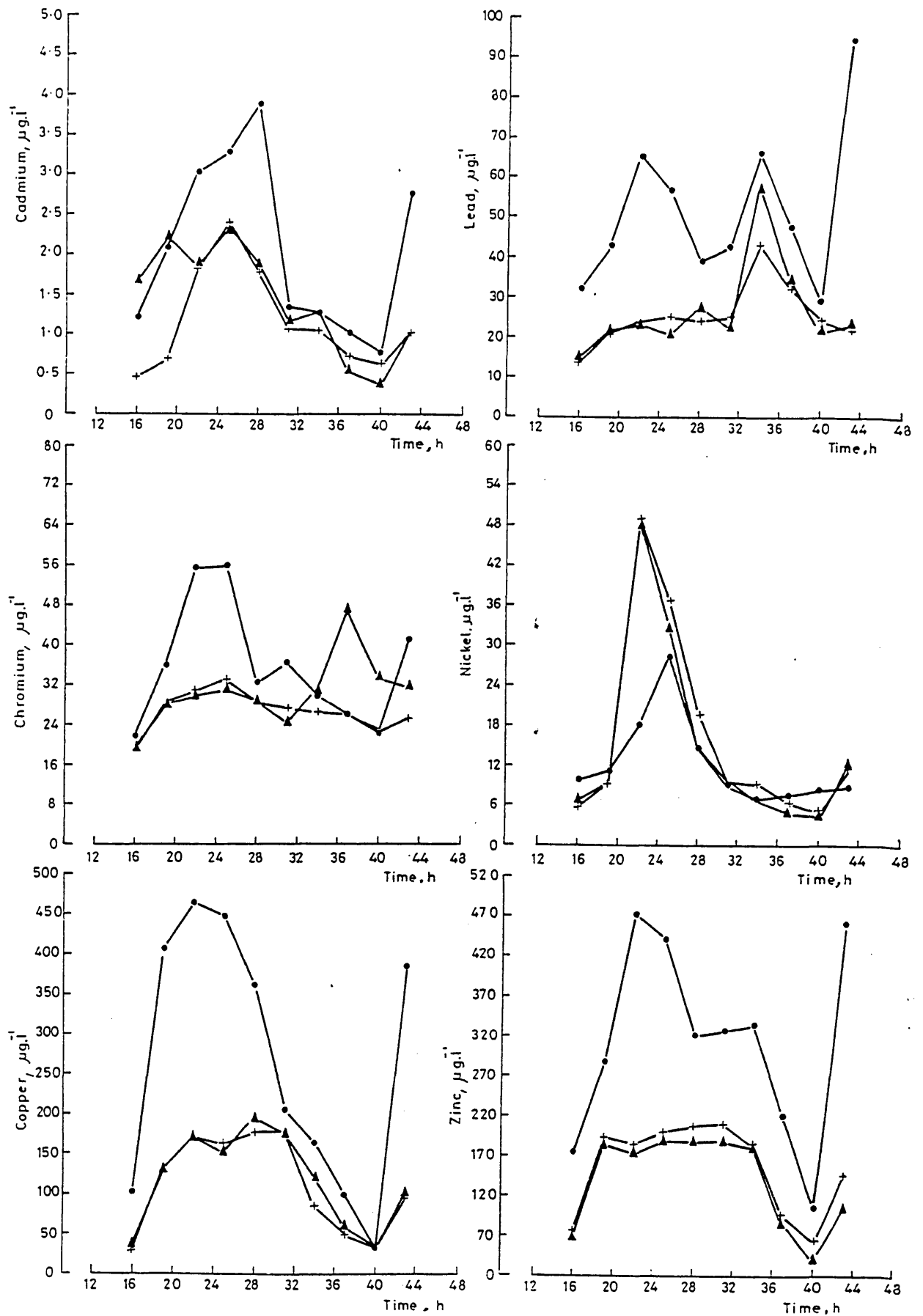


Figure 26 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 1 DWF condition and NTA added at 30 mg l^{-1} .

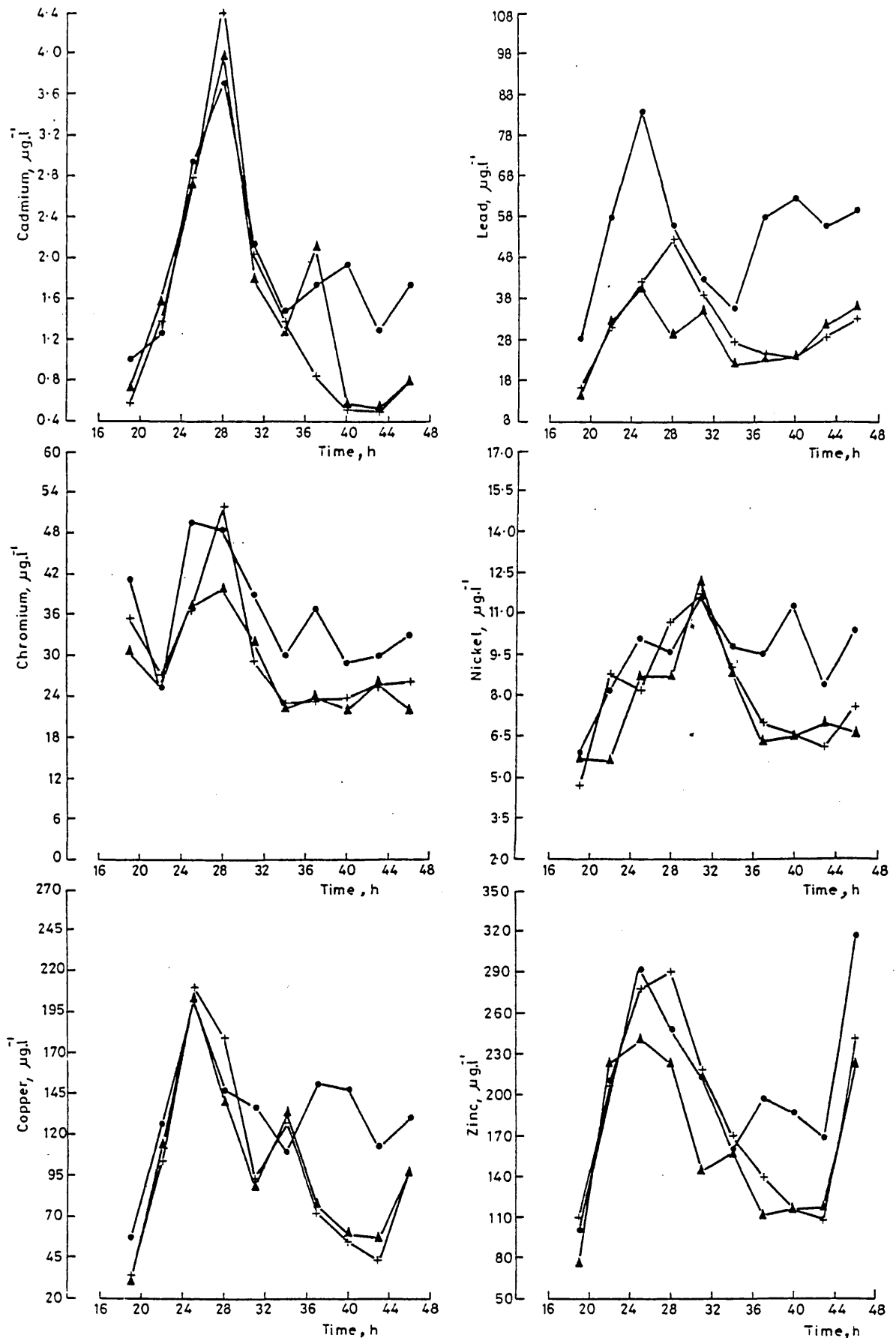


Figure 27 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under 3 DWF conditions and NTA added at 30 mg l^{-1} .

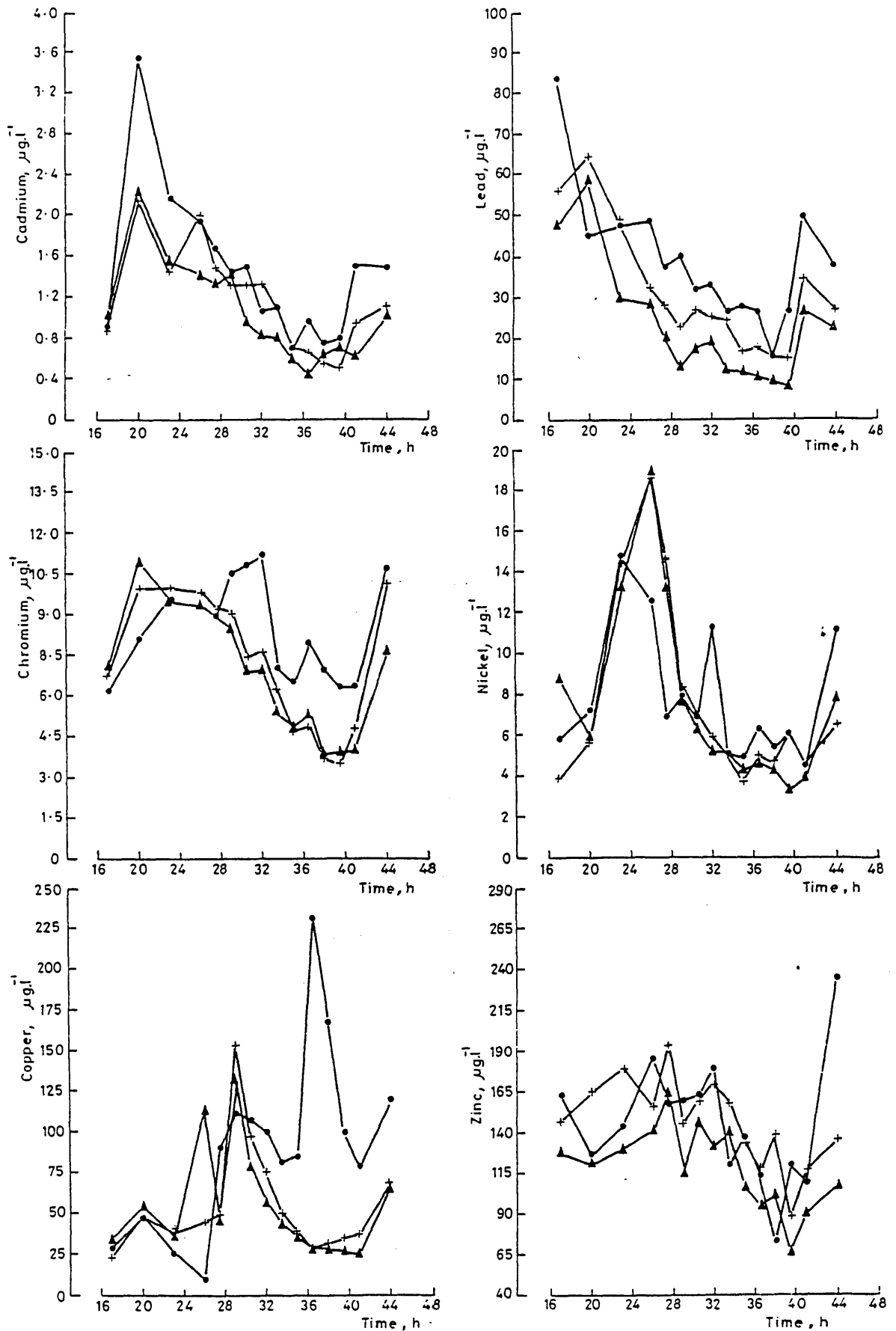


Figure 28 - Variation in heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) from primary sedimentation pilot plant under variable flow condition and NTA added at variable concentrations ($10 - 66 \text{ mg l}^{-1}$).

Table 27 - Heavy metal concentrations during primary sedimentation when NTA was added at 15 or 30 mg ℓ^{-1}

Metal	System	NTA added at 15 mg ℓ^{-1}									NTA added at 30 mg ℓ^{-1}								
		1 DWF			3 DWF			Variable Flow			1 DWF			3 DWF			Variable Flow		
		Mean RSD	Range		Mean RSD	Range		Mean RSD	Range		Mean RSD	Range		Mean RSD	Range		Mean RSD	Range	
Cadmium	Influent	0.37	54	0.11-0.80	0.64	47	0.29-1.29	0.86	26	0.62-1.28	2.07	50	0.77-3.89	1.92	41	1.00-3.72	1.44	49	0.69-3.55
	Effluent Control	0.27	74	0.05-0.72	0.30	66	0.03-0.73	0.81*	27	0.39-1.19	1.43	44	0.37-2.33	1.60	65	0.53-3.98	1.03	44	0.44-2.23
	Effluent Test	0.34	53	0.11-0.70	0.34	49	0.05-0.70	0.92*	25	0.55-1.19	1.17	51	0.46-2.39	1.52	79	0.49-4.44	1.18	42	0.50-2.18
Chromium	Influent	7.8	46	1.7-13.5	25	37	5-36	13.8	44	4.3-25	35.6	33	21.4-55.8	36.3	22	25.4-49.7	8.5	21	6.4-10.9
	Effluent Control	5.9	50	1.9-11.4	17	41	3-25	13.4	49	2.9-24.9	30.2	22	19.3-46.7	28.1	22	21.9-40.0	6.9	32	3.9-10.9
	Effluent Test	5.7	46	1.8-10.8	17	39	3-23	13.1	47	3.1-23.3	26.6	14	18.6-32.9	30.4	29	22.9-52.4	7.2	32	3.5-10.2
Copper	Influent	70	59	14-156	100	44	48-209	57	51	28-112	267	58	33-465	133	27	58-204	100	50	26-232
	Effluent Control	43	48	14-80	40	87	8-122	49	73	14-149	117	48	31-195	100	47	30-203	49*	54	25-133
	Effluent Test	47	45	14-81	39	87	8-121	49	70	15-136	111	52	32-179	102	54	33-211	56*	58	24-154
Lead	Influent	31	40	10-50	38	56	19-101	29	26	20-47	52	36	29-95	54	27	28-84	38	40	15-84
	Effluent Control	26*	66	9-64	13*	55	5-32	22*	37	14-43	29	42	15-58	29	26	14-41	22*	62	8-59
	Effluent Test	28*	55	11-61	14*	49	6-32	24*	38	12-44	26	29	14-43	32	31	16-53	30*	48	15-65
Nickel	Influent	8.7	21	4.9-12	7.5	27	4.8-11.1	6.9	12	5.5-8.1	12	51	7-28	9.5	17	5.9-11.6	7.8	39	4.5-14.8
	Effluent Control	7.4*	26	5.3-11	4.6	26	3.0-6.4	6.5*	15	5.1-8.7	15	90	4-48	7.6	25	5.6-12.2	7.5	57	3.3-19.0
	Effluent Test	8.3*	21	5.2-11	4.4	25	2.7-6.2	6.9*	15	5.3-8.7	16	87	5-49	8.0	25	4.7-11.7	7.9	54	3.7-18.7
Zinc	Influent	145	35	61-264	151	44	50-279	105	25	57-148	314	37	105-471	209	29	100-369	145	26	73-235
	Effluent Control	116*	31	68-203	84	38	61-172	80*	33	36-116	140*	39	40-189	163*	35	75-223	119*	21	66-164
	Effluent Test	133*	32	70-232	106	43	33-211	108*	23	66-137	156*	35	63-210	188*	35	110-291	147*	18	88-194

(*) indicates that the effluent concentration mean values for control and test are different at 5% level of significance.

all values are in $\mu\text{g } \ell^{-1}$

only effluent lead results were statistically different. Except for cadmium high removals for all the other metals were observed during this experiment.

Despite the low metal removal which occurred in the variable flow experiment (Fig. 25) when NTA was dosed at an average concentration of $15 \text{ mg } \ell^{-1}$, cadmium, lead, nickel and zinc were mobilized in the presence of NTA, this was confirmed by the "t" test. Chromium exhibited a peculiar behaviour with its concentration in the influent dropping from 25 to $4.3 \mu\text{g } \ell^{-1}$, suggesting a brief high concentration industrial discharge of this metal into the sewerage system.

When NTA was dosed at $30 \text{ mg } \ell^{-1}$ and at 1 DWF (Fig. 26) nickel and zinc were mobilized by NTA, however only the zinc results were statistically different.

During the experiment at 3 DWF when NTA was added at $30 \text{ mg } \ell^{-1}$ (Fig. 27) zinc was mobilized by NTA which was confirmed by the statistical analysis. Some mobilization was evident for cadmium and lead, however no significant differences were detected.

At variable flow (Fig. 28) when NTA was added at an average concentration of $30 \text{ mg } \ell^{-1}$ ($10\text{--}66 \text{ mg } \ell^{-1}$) all the metals were mobilized in the presence of NTA, however only copper, lead and zinc results were statistically different.

It was evident during this series of experiments that the effluent metal pattern in the test plant did not follow the pattern of metal concentrations in the effluent control which suggests that the effect of NTA depended on the characteristics of the metals in the sewage which varied with time. It is also evident from examination of Figs. 23 to 28 that in general low mobilization in the test plant was found in experiments where the metal removal in the control plant was higher, it may be concluded that other insoluble ligands in the sewage compete strongly with NTA for the metals.

From Table 27 it is evident that cadmium had the lowest values for influent concentration whilst zinc and copper had the highest.

Chromium, lead and nickel were in between. Nickel and lead influent concentrations were nearly constant during the six experiments varying by 30% from the mean values. Cadmium, chromium and zinc presented influent values varying by 70% from the average values. Higher variation was found for copper being 125%.

Percentage removal for the six metals were calculated based on 3 h sampling (method 1) and based on influent composite sample and the amount of metal remaining in the sedimentation tanks at the end of the experiment (method 2). Metal concentration for experiments at variable flow were calculated in the same manner as for suspended solids as described in section 4.4.2. The percentage removals and mass balances were tabulated and are presented in Table 28. The percentage removals calculated by method 2 were always higher than removals calculated by method 1. This indicates that during the 3 h sampling some peaks in influent metal concentration were not sampled resulting in lower values for metal concentration in the influent. Lead and copper during experiments with NTA at 15 mg l^{-1} exhibit low values for their mass balances and the remaining metals have balances in the range 80 - 123%. When NTA was dosed at 30 mg l^{-1} poor balances were observed for all metals with nickel presenting the lowest (47%) and cadmium the highest (156%). As mentioned before no percentage removal (method 2) or mass balances were calculated for experiments at variable flow.

During 1 DWF when NTA was dosed at 15 mg l^{-1} , lead, nickel and zinc were mobilized by NTA and the difference between control and test metal effluent concentrations were significant. This mobilization reduced the removal for these metals and zinc removal decreased from 36 to 11% followed by nickel from 15 to 5% and lead from 18 to 8%.

A reduction in the removal of metals was also observed at 3 DWF when NTA was dosed at 15 mg l^{-1} , however, only lead results were statistically different.

Lead, zinc, nickel and cadmium were mobilized significantly at variable flow. For the last 3 metals higher concentrations in the effluent than in the influent suggested that NTA removed metals from the sludge. During this experiment the removal was very low for all the metals which suggests that the insoluble ligands were present in only low concentrations.

Table 28 - Percentage removal and mass balance for heavy metals during primary sedimentation at different flow conditions when NTA was added at 15 or 30 mg ℓ^{-1}

Metal	Parameter	NTA added at 15 mg ℓ^{-1}						NTA added at 30 mg ℓ^{-1}					
		1 DWF		3 DWF		Variable Flow		1 DWF		3 DWF		Variable Flow	
		Control	Test	Control	Test	Control	Test	Control	Test	Control	Test	Control	Test
Cadmium	% Removal 1	29	10	52	50	3.1*	(-)14.6*	31	44	17	21	30	22
	% Removal 2	64	45	72	88	-	-	47	48	22	21	-	-
	Mass Balance	92	87	96	81	-	-	81	85	156	145	-	-
Chromium	% Removal 1	25	26	34	34	3	4	15	25	23	16	11	8
	% Removal 2	63	68	62	60	-	-	46	56	18	17	-	-
	Mass Balance	82	79	89	88	-	-	73	75	116	107	-	-
Copper	% Removal 1	36	30	57	58	18	7	56	54	24	23	40*	33*
	% Removal 2	100	97	144	140	-	-	33	40	23	27	-	-
	Mass Balance	67	69	55	55	-	-	124	127	103	99	-	-
Lead	% Removal 1	18*	8*	65*	62*	24*	20*	48	51	47	41	35*	16*
	% Removal 2	120	126	150	80	-	-	107	143	45	47	-	-
	Mass Balance	57	54	62	68	-	-	65	55	124	108	-	-
Nickel	% Removal 1	15*	5*	39	42	7*	(-)2*	(-)20	(-)32	20	15	3	(-)1
	% Removal 2	35	34	29	22	-	-	51	49	20	18	-	-
	Mass Balance	80	79	105	112	-	-	49	47	111	105	-	-
Zinc	% Removal 1	36*	11*	44	33	23*	(-)2*	55*	50*	22*	10*	20*	(-)1*
	% Removal 2	40	37	52	46	-	-	40	42	13	15	-	-
	Mass Balance	123	106	98	100	-	-	112	106	153	115	-	-

(-) Indicates metal mobilization

* Indicates that the effluent concentration mean values for Control and test are different at 5% level of significance.

Metal removals during the experiment at 1 DWF when NTA was added at $30 \text{ mg } \ell^{-1}$ are higher than in the experiment at the same hydraulic condition, but at lower NTA dosage. Despite the values for influent COD which were similar, the presence of other ligands could enhance metal removal. In this case only zinc was mobilized but to a lesser extent.

At 3 DWF when NTA was dosed at $30 \text{ mg } \ell^{-1}$ all metals exhibited lower removal and the results calculated by method 1 and method 2 are similar. The influent suspended solids and COD were the highest found during this series of experiments. Only results for zinc in the effluent were statistically different. Since the flow in the Works during this experiment was one of the lowest registered and the weather was very dry, resulting in a very stable flow to the Works, it is possible to conclude that the sewage characteristics were more homogeneous and with a high concentration of organic matter, competition by these organics for the metals probably explains the low mobilization of metals in the presence of NTA in this experiment.

At variable flow nickel presented the lowest removal followed by chromium, removal of all the other metals was in the range 20 - 40%.

Heavy metal concentrations in the sludge solids retained in the tanks when the experiments were finished were determined and these are presented in Table 29. From the examination of Table 29 it is evident that 64% of the results from the metal concentration in the sludge from the test plant are lower than the control confirming that NTA mobilized metals. During these six experiments, zinc and lead were the metals most frequently mobilized, i.e., in 4 out of 6 experiments they showed significant differences in their effluent concentrations between the control and test plant. In two experiments nickel was mobilized in one experiment. , copper and cadmium indicated this effect.

Table 29 - Heavy metal concentration in the sludge solids from the experiments using NTA at 15 or 30 mg ℓ^{-1} and different flow conditions

Metal	NTA added at 15 mg ℓ^{-1}						NTA added at 30 mg ℓ^{-1}					
	1 DWF		3 DWF		Variable Flow		1 DWF		3 DWF		Variable Flow	
	Control	Test	Control	Test	Control	Test	Control	Test	Control	Test	Control	Test
Cadmium	8.2	4.4	14.8	18.6	9.6*	9.7*	20.4	21.1	26.9	26.9	16.1	13.0
Chromium	130.5	141.8	982	968	117	115	311.1	386.3	396	388	89.8	92.6
Copper	2131	2055	6238	3115	1706	1692	1958	2417	2000	2307	1306*	1021*
Lead	938*	953*	4277*	3300*	718*	718*	1245	1685	2672	2777	938*	952*
Nickel	89.4*	85.6*	120.3*	93.8	68.5*	78*	93.2	91.2	121	110.8	69.4	113.5
Zinc	2092*	1912*	8090	7351	1772*	1666*	2370*	2535*	2739*	3150*	1242*	1144*

* indicates that the effluent concentration mean values for Control and Test are different at 5% level of significance
all concentrations are in $\mu\text{g } \ell^{-1}$

4.7 Evaluation of the hydraulic similarity of the two activated sludge pilot plants

As described in Section 3.6.2, the hydraulic characteristics of the two pilot plants were monitored by introducing chloride ions to the inlet pipeline, and measuring the concentration in the mixed liquor and effluent at regular intervals. Chloride concentrations in the plant effluents without any addition of chloride ion at the influent were first measured on six occasions in one day to compare the background concentrations in each plant. Of the six determinations, the test and control plant effluent concentrations (which were approximately $80 \text{ mg } \ell^{-1}$) were equal on three occasions and on the other three occasions differed by $0.5 \text{ mg } \ell^{-1}$ (control plant higher), $1.0 \text{ mg } \ell^{-1}$ (control plant higher) and $2.0 \text{ mg } \ell^{-1}$ (test plant higher). From these results, it was concluded that, for the purposes of the monitoring exercise, it would be sufficient to assume that the background effluent chloride ion concentration in each plant was equal. Consequently, each plant was spiked on separate occasions with 5 g of sodium chloride in the influent and the measured mixed liquor and effluent chloride ion concentrations of that plant were corrected by deducting the measured effluent chloride ion concentration of the plant which was not being dosed. The corrected concentrations were then considered to be representative of the movement of the sodium chloride spike dose through the plant under investigation, and the results of these corrected values for both control and test plants are shown plotted in Fig. 29 for mixed liquor and Fig. 30 for the effluent.

The variation of chloride ion concentration with time in the mixed liquor followed a very similar pattern in each plant with high initial concentrations, reducing exponentially to become asymptotic to the time axis. This pattern would be expected in a completely mixed reactor where the spike dose would be immediately dispersed evenly throughout the mixed liquor, and then be progressively diluted by the subsequent inflow of settled sewage.

The pattern for each plant was also very similar in the effluent, with the chloride ion concentration rising rapidly from zero after about 15 min to a peak between 1.5 and 2 h after introduction of the spike dose. The theoretical average retention time in the pilot plants'

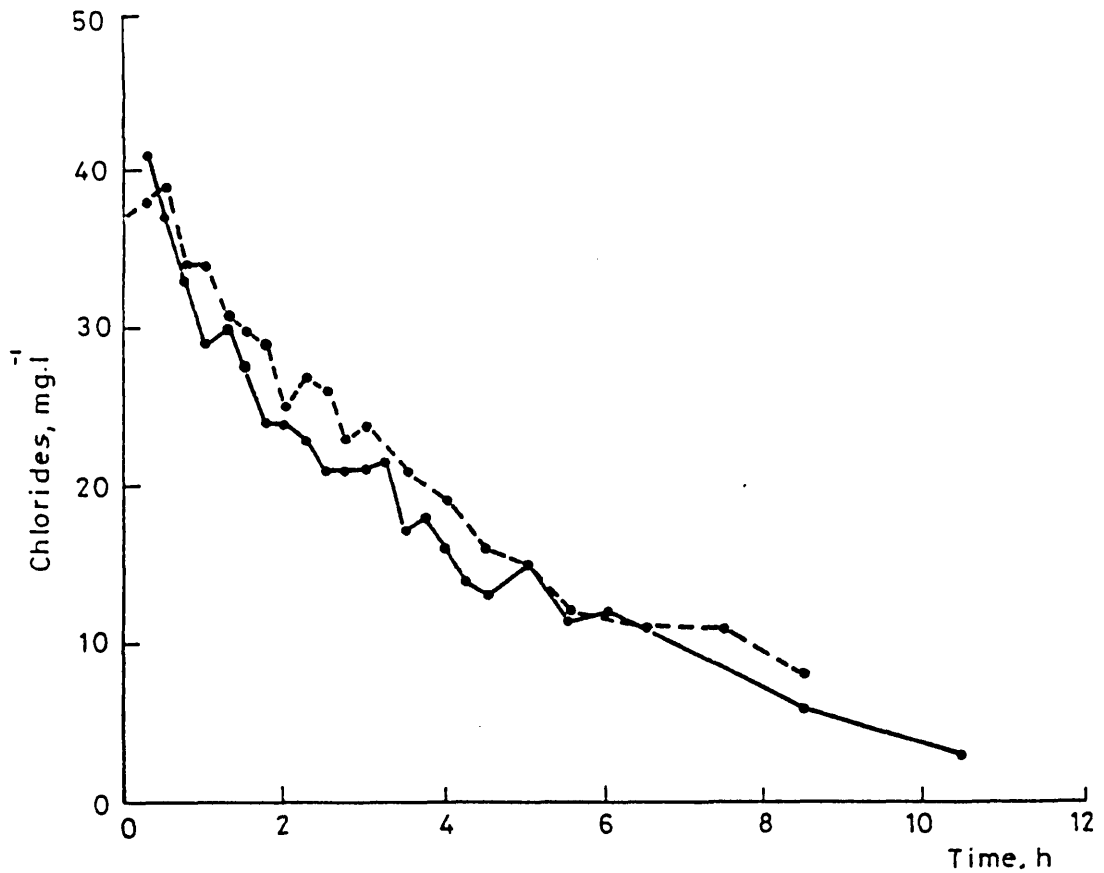


Figure 29 - Chloride concentrations in mixed liquor of the control (---) and test (—) activated sludge pilot plants due to spike dose of 5 g sodium chloride at inlet.

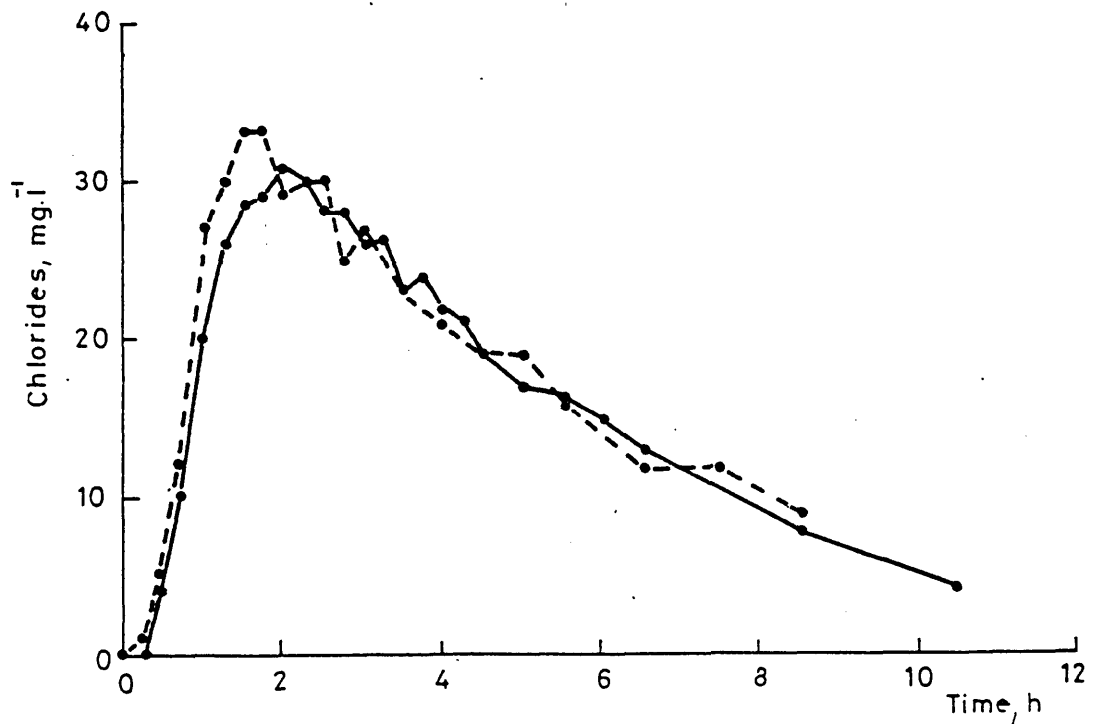


Figure 30 - Chloride concentrations in effluent of the control (---) and test (—) activated sludge pilot plants due to spike dose of 5 g sodium chloride at inlet.

settling tanks is 1.3 h based on a 20 ℓ capacity and a flow rate of 15 $\ell \text{ h}^{-1}$. On comparing Fig. 29 and 30, it can be seen that, for both plants, a particular concentration of chloride ion in the effluent lags the same concentration in the mixed liquor consistently by about 1 h which is close to the 1.3 h average retention time and suggests that there is little short circuiting in the system.

It may be concluded, therefore, that hydraulically the two plants closely correspond to one another in performance and each operates in the manner expected by the principles of the design of the units.

A similar experiment involving the continuous dosing of sodium chloride to the test plant was also conducted and the results are presented in section 4.9.

4.8 Metal removal during the activated sludge process

The objective of this work was to study the biodegradation of NTA under a range of operational conditions and to determine its influence on heavy metal removal. In all ten paired experiments have been undertaken at different sludge ages, influent heavy metals concentrations and influent NTA concentrations. The data for metal removal from the control plant during six of these experiments (3 sludge ages and two concentrations of influent heavy metals) have been tabulated and treated separately to permit the removal of metals alone to be evaluated. Necessarily these control data are repeated in section 4.10.4 for comparative purposes.

4.8.1 Influence of sludge age on heavy metal removal

Heavy metal removal efficiencies were determined at sludge ages of 4, 9 and 12 d. Additionally removals were determined at two influent concentrations for each metal; the higher concentration being obtained by adding soluble metal salts to the settled sewage. Removals for both normal and elevated concentrations are shown in Table 30. Removals of nickel were consistently poor, being in the range 11 - 36%, while the removals of copper and lead were generally good. The removals of cadmium, chromium and zinc were also relatively efficient generally being in the range 40 - 80%. Removals at the lower influent concentrations

Table 30 - Heavy metal removal efficiency from spiked and non-spiked settled sewage at sludge ages of 4, 9 and 12 d.

Sludge age d	Metal concentration	Cadmium conc. $\mu\text{g l}^{-1}$	%R	Chromium conc. $\mu\text{g l}^{-1}$	%R	Copper conc. $\mu\text{g l}^{-1}$	%R	Lead conc. $\mu\text{g l}^{-1}$	%R	Nickel conc. $\mu\text{g l}^{-1}$	%R	Zinc conc. $\mu\text{g l}^{-1}$	%R
4	Normal	0.43	68	42.0	10	46.4	81	16.6	66	21.0	11	88	41
9		1.40	33	5.6	55	56.2	70	24.0	80	17.6	36	156	51
12		2.98	8	5.8	49	65.9	74	29.3	32	20.8	22	127	39
4	Metals added	7.13	60	112	46	176	83	56.3	69	173	16	545	55
9		12.2	80	80	62	137	82	64.3	77	119	16	576	68
12		8.4	60	35.6	68	138	84	66.2	82	94.7	33	675	40

Table 31 - Mean values of suspended solids, COD, SVI and food to micro-organism ratio at sludge ages of 4, 9 and 12 d.

Sludge age d	Metal conc.	Suspended Solids		COD			SVI g ml^{-1}	F/M*
		Mixed Liquor mg l^{-1}	Effluent mg l^{-1}	Influent mg l^{-1}	Effluent mg l^{-1}	Removal %		
4	low	1641	10.5	194	46	76	391	0.63
9	low	2934	4.6	231	48	79	71	0.46
12	low	3687	17.0	240	49	80	215	0.36
4	high	1414	3.0	285	57	80	104	0.70
9	high	2640	13.0	245	56	77	129	0.60
12	high	3742	13.0	270	66	76	126	0.33

* food to micro-organism ratio calculated in terms of COD and MLVSS

were more variable than when metals were added. In particular, the unusually low removals of cadmium and chromium of 8 and 10% respectively coincided with significantly higher concentrations of these metals in the sewage, suggesting that shock loads of heavy metals may result in a significant decrease in removal efficiency. However, when metals were added to the settled sewage the percentage removals of cadmium, chromium, copper and zinc all appeared to be higher than the removals at low influent concentrations. This may have been a result of the changes in metal speciation when heavy metals were added.

The mean concentrations of MLSS, effluent suspended solids, influent and effluent COD, SVI and F/M (food to micro-organism ratio calculated in terms of COD and MLVSS) at each sludge age are shown in Table 31. For both normal and elevated concentrations of metals the MLSS concentrations increased with increasing sludge age, the food to micro-organism ratio decreased with increasing sludge age, while the effluent COD and COD removals remained fairly constant. Thus any trends in heavy metal removals in response to the sludge age may have been due to variations in one or more of the parameters related to sludge age.

In contrast to those parameters which showed definite correlations with sludge age, the mean values of effluent suspended solids and SVI were more variable and did not appear to be related to sludge age. Particularly low values of effluent suspended solids occurred at the 9 d sludge age when no metals were added, and at 4 d sludge age when metals were added. In the former instance, the low effluent suspended solids concentration coincided with a particularly low SVI value, indicating that the quality of the effluent was related to an efficiently settling sludge. When metals were not added to the system, optimum removals of chromium, nickel, lead and zinc coincided with the lowest effluent suspended solids concentrations, while the poorest removals of lead and zinc coincided with the highest effluent suspended solids concentration. This suggests that the removals of lead, in particular, and some other metals may be determined to some degree by the concentrations of particulate forms escaping in the effluent.

4.8.2 Influence of sludge age on heavy metal accumulation by mixed liquor solids

The accumulation of heavy metals by the mixed liquor under steady state conditions at each sludge age was determined as a function of the

biomass concentration and the quantity of metal in the influent settled sewage. The accumulation factors were expressed as mg of metal accumulated per g of biomass (MLSS) per mg ℓ^{-1} of metal in the influent settled sewage. The values for the accumulation of metals are shown in Table 32.

When metals were added to the settled sewage, there was a general trend, except in the case of zinc, to a greater degree of adsorption by the biomass with increasing sludge age. However, the same phenomenon was not observed when metals were not added to the system, and in particular, the accumulation of cadmium by the mixed liquor decreased with increasing sludge age. The greatest uptake of all metals occurred at the 12 d sludge age when heavy metals were added, whereas only zinc was accumulated to the greatest extent at the 12 d sludge age under normal metal loadings, while the greatest uptake of chromium, copper, nickel and lead occurred at the 9 d sludge age.

A comparison of the mean values for the uptake of heavy metals under normal and elevated influent concentrations reveals that cadmium, copper and lead were more readily accumulated when metals were added, whereas chromium, nickel and zinc were accumulated to the same extent, relative to the influent heavy metal concentrations. This suggests that the availabilities of the former three metals may have been influenced by the chemical forms in the settled sewage, in contrast to the latter three metals, whose accumulation by the biomass may have been controlled by the equilibrium between adsorbed and free metal. The following series of decreasing order of uptake, based on the mean values from Table 32, were obtained:

low metal concentration $\text{Cu} > \text{Pb} > \text{Cr} > \text{Zn} > \text{Cd} > \text{Ni}$

high metal concentration $\text{Pb} > \text{Cu} > \text{Cd} > \text{Cr} > \text{Zn} > \text{Ni}$

Although the degree of accumulation of some metals may have been influenced by their concentrations and chemical forms in the settled sewage, these series indicate that copper and lead were accumulated to the greatest extent, while zinc and nickel were associated with the biomass to only a limited extent. This is in general agreement with the relative removal efficiencies observed for these metals shown in Table 30.

Table 32 - Accumulation factor of heavy metals by activated sludge
at sludge ages of 4, 9 and 12 d.

Sludge age d	Metal concentration	MLSS mg ℓ^{-1}	Accumulation factor *					
			Cadmium	Chromium	Copper	Lead	Nickel	Zinc
4	Normal	1641	4.9	3.3	4.8	6.0	1.6	3.1
9		2934	3.1	5.7	10.6	7.8	2.0	2.8
12		3687	1.6	5.3	8.8	3.7	1.7	4.6
4	Metals added	1414	4.1	3.8	7.7	9.0	1.1	3.5
9		2640	5.8	4.0	9.7	7.8	1.6	3.2
12		3742	7.6	6.7	9.7	10.7	2.4	3.7

* mg of metal accumulated per g of MLSS per mg ℓ^{-1} of influent metal

Table 33 - Heavy metal solubilities in settled sewage and final effluents
at sludge ages of 4, 9 and 12 d.

Sludge age d	Sample type	Mean % Solubility					
		Cadmium	Chromium	Copper	Lead	Nickel	Zinc
-	Settled sewage	15	-	37	4	100	1
4	Final effluent	29	5	100	22	81	2
9		61	13	100	14	91	8
12		30	1	27	12	100	10

4.8.3 Influence of sludge age on heavy metal solubilities in final effluent

Four samples each of settled sewage and final effluent were taken when the pilot plant had attained steady state conditions at each sludge age. Samples were taken during experiments when heavy metals were added to the settled sewage. Heavy metal solubilities were determined by membrane filtration (section 3.5). The mean values for metal solubilities in the influent and the effluents at each sludge age are shown in Table 33. Data were not available for chromium solubility in the settled sewage.

Cadmium, lead and zinc solubilities in the final effluents at all sludge ages were all higher than their percentage solubilities in the settled sewage. Copper solubility in the effluent at sludge ages of 4 and 9 d was also much higher than in the settled sewage, while nickel solubilities were high in all samples, ranging from 81 - 100%. Lead, zinc and chromium had the lowest solubilities in the effluents of 12 - 22%, 2 - 10% and 1 - 13% respectively, indicating that these metals were predominantly associated with poorly settleable particulates. The high solubility of nickel reflected its poor removal, indicating that it had a very low affinity for particulates while the high copper solubility may have been due to soluble forms of the metal leaving the system as a result of their unavailability for uptake by the biomass.

4.9 Estimation of the removal of NTA in activated sludge by adsorption onto mixed liquor solids

To assess the ability of activated sludge to adsorb the NTA onto the mixed liquor and to determine the amount of NTA removed by this mechanism a series of experiments were undertaken as described in section 3.3. Mixed liquor samples were collected from the pilot plant control aerator and from the aerator in the Hogsmill Valley Sewage Treatment Works. Some samples were diluted with final effluent to achieve the desired value for MLSS. Jar tests were undertaken with NTA added at $15 \text{ mg } \ell^{-1}$. Samples were collected at 2, 5, 8, 11 and 20 min intervals and analysed for NTA after filtration. The NTA adsorption increased during the first 8 min and after that decreased. Therefore the values for 8 min samples were used to calculate the percentage adsorbed in each experiment. The results for each experiment and the MLSS characteristics

are presented in Table 34. Mixed liquor from the Works were tested on two different days (Experiments 1 and 3) and they exhibited approximately the same MLSS concentration, however the percentage adsorbed was twofold higher in experiment 2. When NTA was added to mixed liquor from different sources but having the same concentration (experiments 2 and 3) again different degrees of adsorption were shown. Temperature during experiment 3 was higher than experiment 2 however the difference (3.75°C) was not the only factor to explain the reduction of 60% in the adsorption. When mixed liquor from the Works was spiked with metal (experiment 5) the adsorption was marginally higher than the original (experiment 4), but with only one observation it is not possible to determine if this was significant. As it was expected for mixed liquor from the same source there was a correlation between mixed liquor concentration and percentage of NTA adsorbed. From the experiments it is clear that mixed liquor from different sources has different adsorption capacities.

The mixed liquor characteristics during the experiments mentioned before probably was altered because of the static conditions, therefore adsorption of NTA onto the mixed liquor was examined under dynamic conditions. Following the stabilization of the pilot plant's mixed liquor at 4 days sludge age, NTA was introduced to the test plant to give a nominal concentration of $7.5 \text{ mg } \ell^{-1}$ in the influent sewage. The NTA concentration in the test plant effluent was then determined at hourly intervals over a period of 12 h from the time that dosing commenced. From the measured flow of settled sewage to the test plant and the volume of NTA solution used over the duration of the test, it was possible to determine the percentage of the actual average influent NTA concentration that was discharged in the effluent at any particular time. The variation of this percentage with time is shown in Fig. 31.

As mentioned in section 4.7 an experiment was also conducted on the test plant to monitor its hydraulic characteristics using a continuous dose of sodium chloride solution to give $100 \text{ mg } \ell^{-1}$ chloride ion concentration in the effluent to the plant at $15 \ell \text{h}^{-1}$ sewage flow. The control plant effluent chloride ion concentration was again used as a standard to enable the concentration in the test plant effluent solely due to the added sodium chloride solution to be determined.

Table 34 - Percentage of NTA adsorbed onto mixed liquor

Parameter	Experiment 1 ML from Works	Experiment 2 ML from Works	Experiment 3 ML from Pilot Plant diluted	Experiment 4 ML from Works	Experiment 5 ML from Works spiked with metals
MLSS conc mg ℓ^{-1}	2579	2767	2767	1487	1487
% Adsorbed	18	45	18	13	15
Temperature $^{\circ}\text{C}$	16.5 - 17.5	14.5 - 18.6	20 - 20.5	18.3 - 18.6	18.3 - 18.6

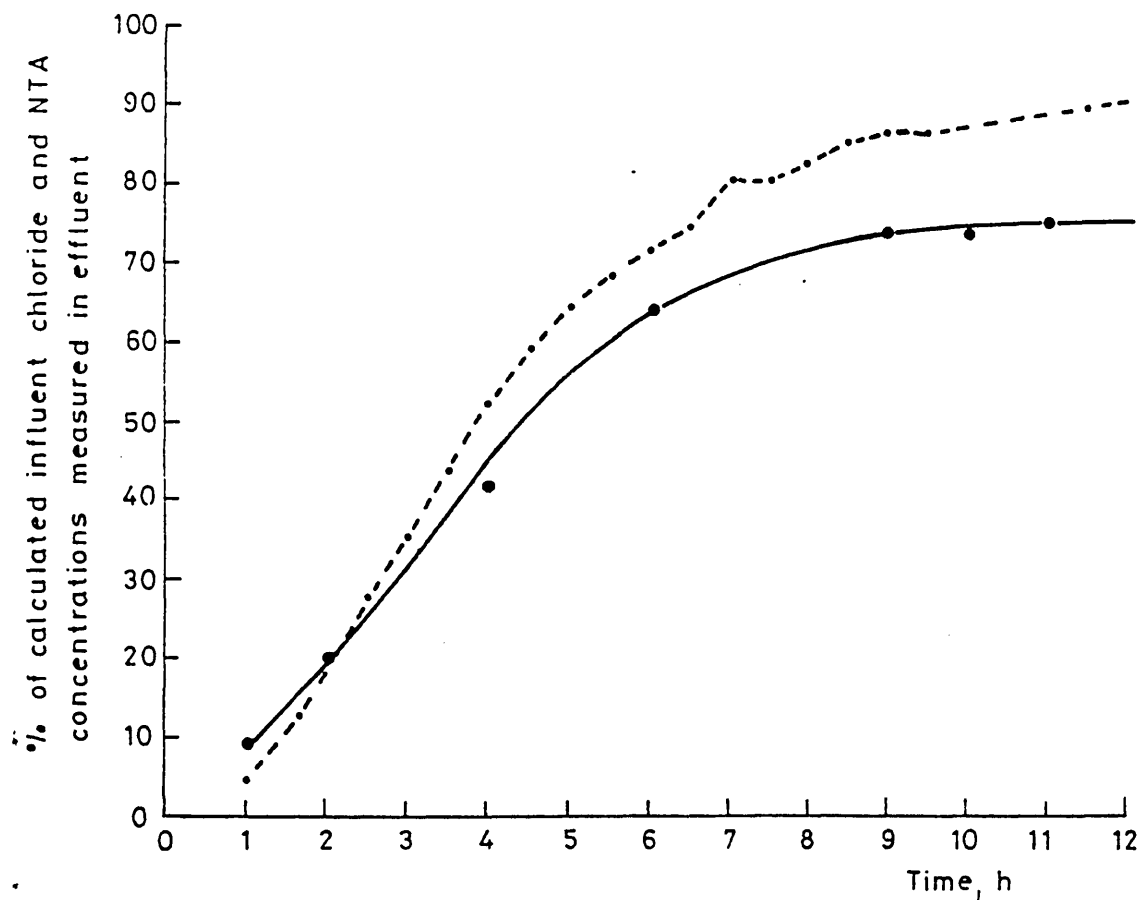


Figure 31 - Percentage of calculated influent NTA (—●—) and chloride (---●---) concentrations measured in test plant effluent at various times after commencement of continuous dosing.

The percentage of the average influent concentration reaching the effluent at any given time was determined in the same manner as described above for the NTA, and the results are shown in Fig. 31.

During the course of the NTA and the chloride experiments the recirculation ratio was maintained at a 1:1, but the sludge wastage from the aerator was stopped. From the examination of Fig. 31 it can be seen that the average profile of the NTA curve is similar to the curve for chloride ion concentration. The NTA curve shows some flattening after 9 h. As the test plant was emptied and cleaned before the start of the experiment and filled with activated sludge from the Works, which was unacclimatized to NTA it is reasonable to assume that biodegradation had not started within the first 9 h after

commencement of dosing with NTA. So it is possible to conclude that an adsorption of 25% was found for NTA during the start of the acclimatization period with an MLSS around $1600 \text{ mg } \ell^{-1}$.

4.10 An investigation of some of the factors which might influence the acclimatization of the activated sludge process to NTA

The onset of NTA biodegradation is preceded by a variable period of acclimatization. Whilst it is probable that the onset of acclimatization is dependent on the chance inoculation of bacteria with the ability to biodegrade NTA, once acclimatization commences the rate at which it proceeds to completion is probably dependent upon operational parameters which control the development of the bacterial population. The effect of sludge age, heavy metal concentrations and NTA concentration on the process of acclimatization have been studied. Examination of the acclimatization periods from those experiments reported in Section 3.2.2 in which these parameters were varied permits their effects on the process to be studied.

Before each experiment the pilot plant was emptied and cleaned and mixed liquor from the Hogsmill Valley Works was used as a seed, this was not acclimatized to NTA. Thus it can be assumed that none or only a small number of NTA biodegrading bacteria were present when the experiments commenced. The system was assumed to be acclimatized when the NTA effluent concentration reached negligible values.

4.10.1 Effect of sludge age on the biodegradation of NTA during the acclimatization

The acclimatization was studied in three experiments when the pilot plant was operated at sludge ages of 4, 9 and 12 d using settled sewage with low metal concentrations and when NTA was added at $7.5 \text{ mg } \ell^{-1}$. NTA influent and effluent concentrations were monitored during the acclimatization and the results are presented in Fig. 32.

When NTA was added to the system operating at 4 d sludge age a maximum value of $6.2 \text{ mg } \ell^{-1}$ of NTA was detected in the effluent 12 h after the addition had started. After that a gradual reduction in

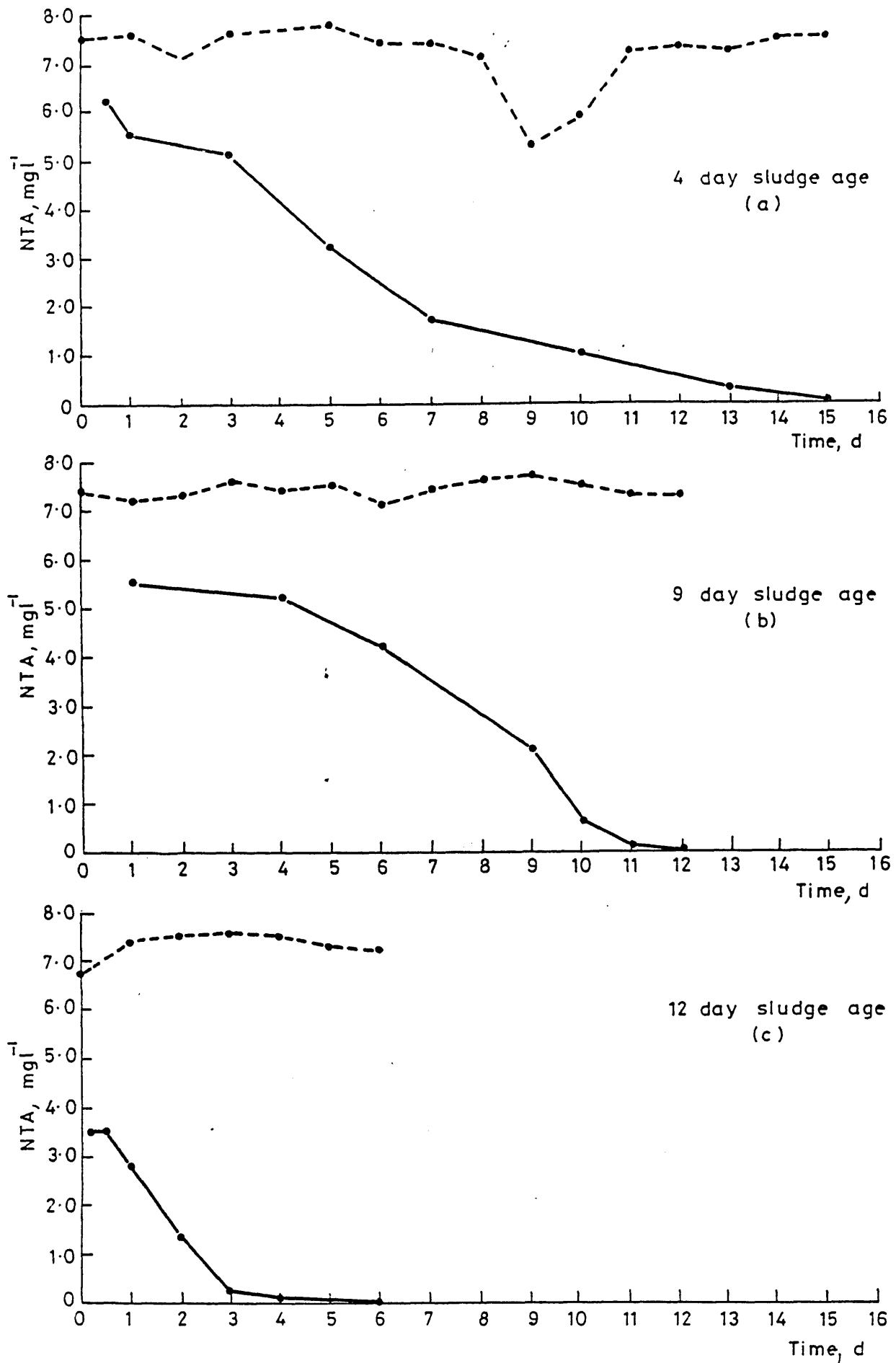


Figure 32 - NTA concentration in influent (----) and effluent (•) in the activated sludge pilot plant at 4, 9 and 12 d sludge ages and low metal concentrations in the influent when NTA was dosed at 7.5 mg l^{-1} during acclimatization.

the NTA effluent concentration was observed until by the 15 d the NTA concentration in the effluent was negligible. When the pilot plant was operated at 9 d sludge age, $5.5 \text{ mg } \ell^{-1}$ of NTA was measured in the effluent 24 h after the dosage commenced and a continuous reduction in NTA effluent concentrations was observed reaching negligible values 12 d after the experiment had started. At 12 d sludge age a maximum value of $3.5 \text{ mg } \ell^{-1}$ was detected in effluent 6 h after the experiment had commenced and 97% of the influent NTA was biodegraded within 3 d. The complete biodegradation was achieved in 6 d. These results are summarised in Table 35.

Table 35 - Acclimatization time for NTA in activated sludge at low metal and low NTA influent concentrations and at different sludge ages.

Sludge age d	Acclimatization time d
4	15
9	12
12	6

For these experiments at 4, 9 and 12 d sludge age the wastage was 15, 6.67 and $5 \ell \text{d}^{-1}$ respectively (section 3.2.3.2.2) which represents 24, 11 and 8% of the aerator volume. Thus it would be expected that at 4 d sludge age it would take longer for the system to achieve the appropriate number of NTA biodegrading bacteria to achieve complete biodegradation since the higher wastage would reduce their population size drastically. At 12 d sludge age, when only 8% of the total volume of the aerator was discharged each day, the necessary number of bacteria to biodegrade the NTA completely was achieved in shorter time. Average values for mixed liquor suspended solids during these experiments were 1514, 3049 and $3536 \text{ mg } \ell^{-1}$ at 4, 9 and 12 d sludge age respectively. Since the disappearance of NTA during the first 12 h of these experiments was most likely due to adsorption onto the mixed liquor it would be expected that the higher the MLSS the greater would be the removal of NTA in the first 12 h. This is supported by the removals

observed in the first 12 h during the experiments at 12 and 4 d sludge age when removals of 48 and 17% respectively were observed. At 9 d sludge age the removal during the first 12 h was not determined. Acclimatization to NTA is more rapid at higher sludge ages because the lower wastage rate favours the development of the new NTA degrading bacteria and removal of NTA is further enhanced by increased adsorption as a result of the high MLSS concentration.

4.10.2 Effect of heavy metal influent concentration on the acclimatization of the activated sludge pilot plant to NTA

Two pairs of experiments were used to study the effect of elevated heavy metal concentration on the acclimatization of NTA at different sludge ages (4 and 9 d) when the pilot plant was fed with settled sewage or settled sewage spiked with heavy metals, both containing 15 mg l^{-1} of NTA.

When the system was dosed with 15 mg l^{-1} of NTA at 4 d sludge age and the metal content of the settled sewage was low, the time for acclimatization was 20 d (Fig. 33). When the same conditions were maintained except that the heavy metal concentration in the experiment was increased (high metal) no acclimatization was observed over the 18 d period of study (Fig. 34). In this experiment the effluent NTA concentration was approximately 10 mg l^{-1} during the 18 d which represented a reduction of 32% of the incoming NTA to the system. However after 18 d when the sludge age was increased to 6 d biodegradation commenced and in 10 d complete biodegradation of NTA was achieved.

During the experiment when NTA was added at 15 mg l^{-1} in the pilot plant operating at 9 d sludge age and receiving settled sewage with low metal content, complete biodegradation occurred 15 d after the experiment had commenced. However when the same conditions were maintained and heavy metals were added to the settled sewage it took 25 d for the system to acclimatize to NTA. The results of these experiments are tabulated in Table 36.

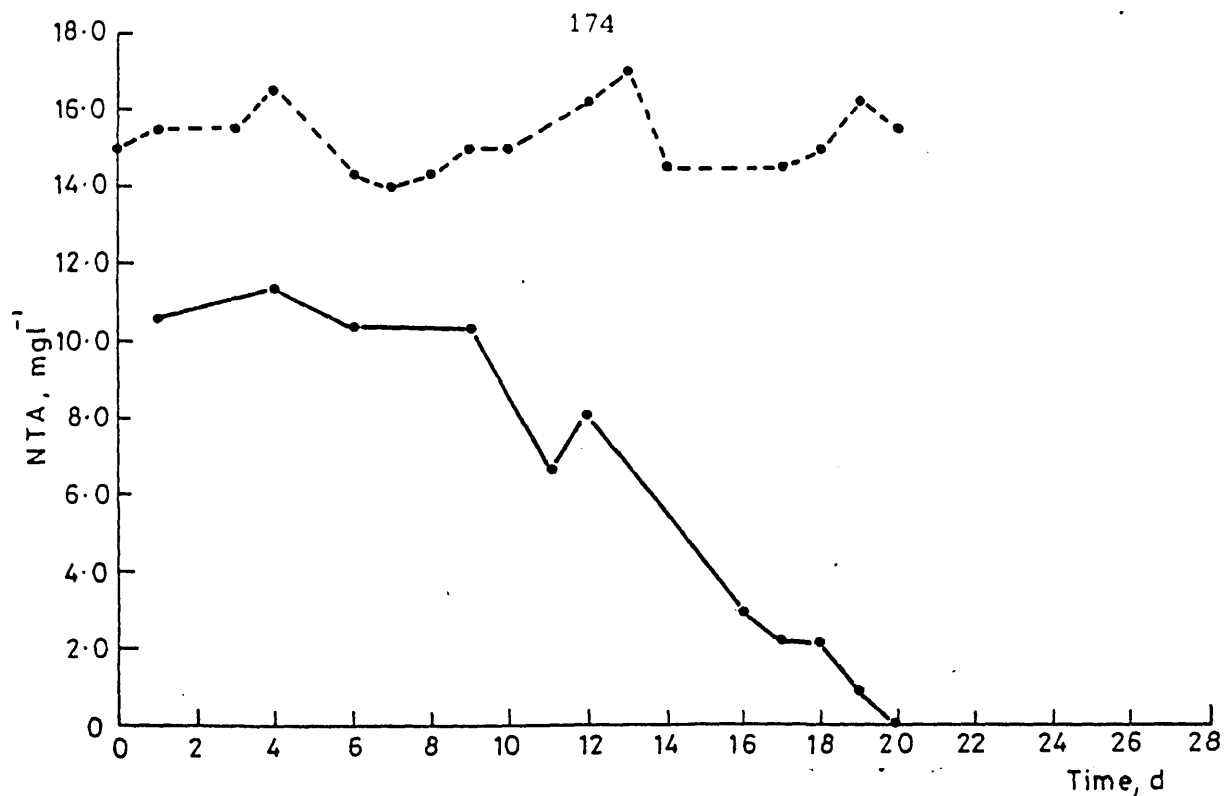


Figure 33 - NTA concentrations in influent (----) and effluent (—●—) in the activated sludge pilot plant at 4 d sludge age and low metals in the influent when NTA was dosed at $15 \text{ mg } \ell^{-1}$ during acclimatization.

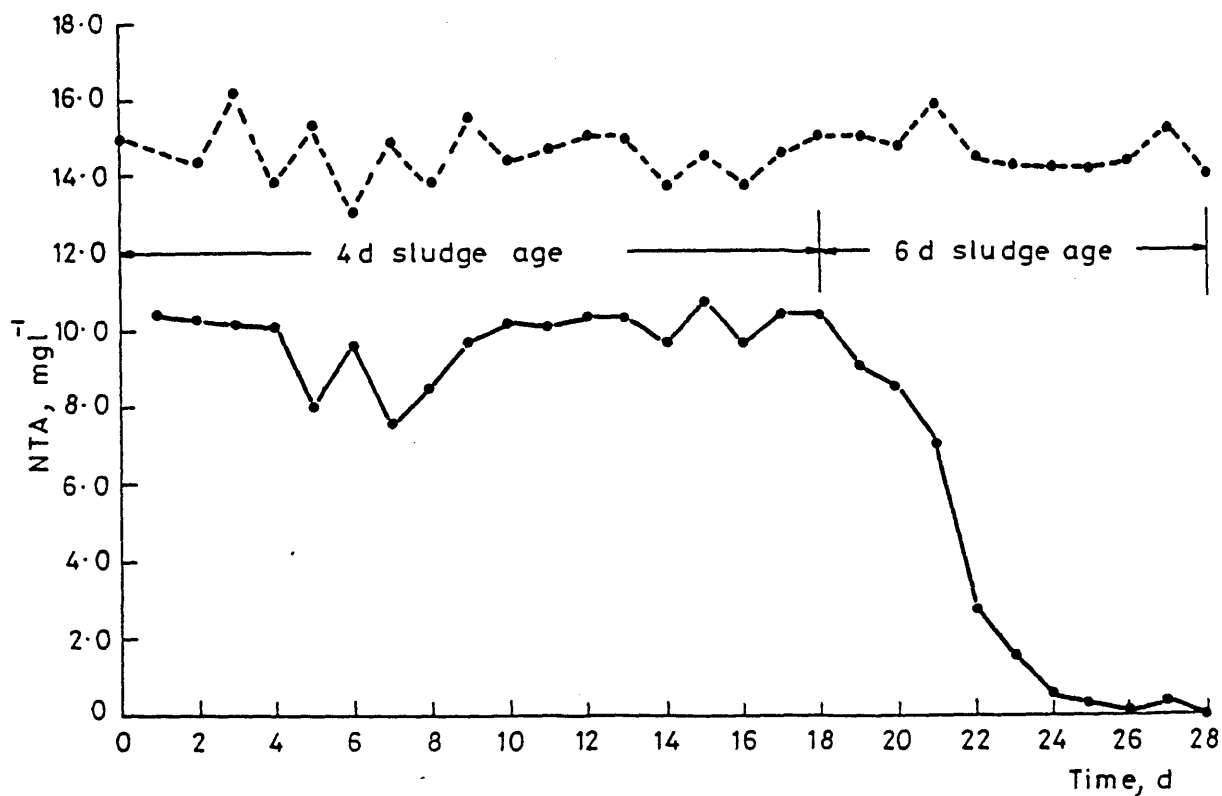


Figure 34 - NTA concentrations in influent (----) and effluent (—●—) in the activated sludge pilot plant at 4 and 6 d sludge ages and high metals in the influent when NTA was dosed at $15 \text{ mg } \ell^{-1}$ during acclimatization.

Table 36 - Acclimatization time for NTA in activated sludge at different sludge ages and different influent metal concentrations when NTA was added at $15 \text{ mg } \ell^{-1}$.

Sludge age d	Influent metal concentration	Acclimatization time d
4	low	19
4	high	>18*
9	low	15
9	high	25

* No acclimatization during the 18 d of study.

It is evident from the observations in Table 36 that the system with high influent metal concentrations required more time to acclimatize to NTA presumably as a result of the formation of less readily degradable complexes.

4.10.3 Effect of NTA influent concentration on the biodegradation of NTA during the acclimatization

To assess the effect of NTA influent concentration on the acclimatization of the pilot plant to NTA two pairs of experiments were undertaken when the plant was fed with settled sewage without addition of heavy metals. In each pair of experiments the sludge age was kept the same but two concentrations (7.5 and $15 \text{ mg } \ell^{-1}$) of NTA were added. The acclimatization periods in each experiment were tabulated and are presented in Table 37

Table 37 - Acclimatization time for NTA in activated sludge at low metal concentration and different sludge ages and influent NTA concentrations

Sludge age d	NTA influent conc. $\text{mg } \ell^{-1}$	Acclimatization time d
4	7.5	15
4	15.0	20
9	7.5	12
9	15.0	16

When NTA was added at low concentration ($7.5 \text{ mg } \ell^{-1}$) in a system operating at 4 d sludge age and low influent metal concentration 15 d were necessary to achieve complete biodegradation of NTA. This time was increased to 20 d when the NTA dosage was doubled ($15 \text{ mg } \ell^{-1}$). For experiments at 9 d sludge age an increase in NTA influent concentration from $7.5 \text{ mg } \ell^{-1}$ to $15 \text{ mg } \ell^{-1}$ increased the acclimatization time from 12 to 16 d.

It would appear from the results that the time required for acclimatization to NTA is proportional to the NTA influent concentration. The results in Table 37 are consistent with the conclusion drawn from section 4.10.1 since an increase in sludge age reduced the time required for acclimatization to NTA.

4.10.4 Effect of NTA on heavy metal removal during the acclimatization in the activated sludge process

To assess the effect of NTA on heavy metal removal during the acclimatization phase samples were collected for metal analysis in two experiments, one with low and one with high influent metal concentrations. During these experiments the sludge age was maintained at 9 d and NTA was dosed at $7.5 \text{ mg } \ell^{-1}$. Composite samples of influent, effluent control and effluent test were prepared daily as described in section 3.2.6. Operational parameters for the experiments in study are included in Table 38. The results of the metal analysis are presented in Figs. 35 and 36. Mean values, relative standard deviation, range and percentage mobilization as well as percentage removal and mean balances for the heavy metals during the acclimatization period were calculated and are presented in Table 39. Mean values, relative standard deviation and range for heavy metal concentrations in mixed liquors are presented in Table 40.

The performance parameters of the two pilot plants during the experiment at low influent metal concentrations can be seen in Table 38. Mixed liquor suspended solids and mixed liquor volatile suspended solids were lower in the test plant. These differences were statistically significant, however the performance of the plants in terms of COD removal, mixed liquor settleability (SVI) and suspended solids in the effluent were comparable. Values for pH were higher in the test plant and the difference was statistically significant.

Table 38 - Values of the treatment parameters for experiments with low and high heavy metals in the influent, at 9 d sludge age when NTA was added at $7.5 \text{ mg } \ell^{-1}$ during acclimatization

Parameter	System	Low heavy metals			High heavy metals		
		mean	RSD %	range	mean	RSD %	range
MLSS $\text{mg } \ell^{-1}$	Aerator C	3345*	4.6	3085-3605	2898	13	2325-3285
	Aerator T	3049*	12	1920-3435	2949	4.8	2785-3155
MLVSS $\text{mg } \ell^{-1}$	Aerator C	2965*	4.5	2760-3150	2612	16	2035-2915
	Aerator T	2629*	12	1675-2915	2735	6.4	2495-2915
SS $\text{mg } \ell^{-1}$	Effluent C	8.5	157	1- 50	7.6	25	5.0-9.5
	Effluent T	5.8	79	1- 15	8.5	31	5.0-11
SVI ₁ ml g^{-1}	Aerator C	90.3	34	65- 180	295	21	202-374
	Aerator T	94.1	35	69- 190	286	15	211-321
pH	Influent	7.57	1.5	7.35-7.75	7.56	0.3	7.54-7.60
	Effluent C	7.53*	1.1	7.34-7.62	7.43	0.4	7.39-7.45
	Effluent T	7.59*	1.3	7.39-7.76	7.41	0.5	7.38-7.46
NH ₃ $\text{mg } \ell^{-1}$ as N	Influent	22	30	13- 32	33	21	23- 39
	Effluent C	0.15	41	0.1-0.28	15	22	12- 20
	Effluent T	0.14	51	0.1-0.30	15	22	11- 19
COD $\text{mg } \ell^{-1}$	Influent	214	21	145- 270	221	7.8	200- 242
	Effluent C	43	17	32- 52	51	22	40- 67
	Effluent T	47	11	39- 53	43	10	38- 49
F/M [†]	Aerator C	0.46	31	0.27-0.66	0.36	11	0.32-0.40
	Aerator T	0.38	22	0.23-0.47	0.37	11	0.33-0.41
Ortho Phosphate $\text{mg } \ell^{-1}$ as P	Influent	4.91	18	3.76-6.56	9.32	11	8.24-10.4
	Effluent C	5.04	21	2.76-6.18	9.05	5	8.59-9.50
	Effluent T	4.74	21	2.76-5.96	9.61	4	9.18-10.0
Total Inorganic Phosphate $\text{mg } \ell^{-1}$ as P	Influent	6.13	11	4.63-6.90	9.50	9	8.60-10.4
	Effluent C	5.95	16	4.34-8.05	9.85	4	9.40-10.3
	Effluent T	5.88	20	3.66-8.01	10.1	4	9.74-10.5

[†] Based on COD values for influent and effluents

* Indicates that the means are statistically different at 5% level of significance

This would be anticipated since the sodium from the NTA salt increased the alkalinity of the sewage (Appendix IX) this would influence the pH depending on the buffering capacity of the sewage.

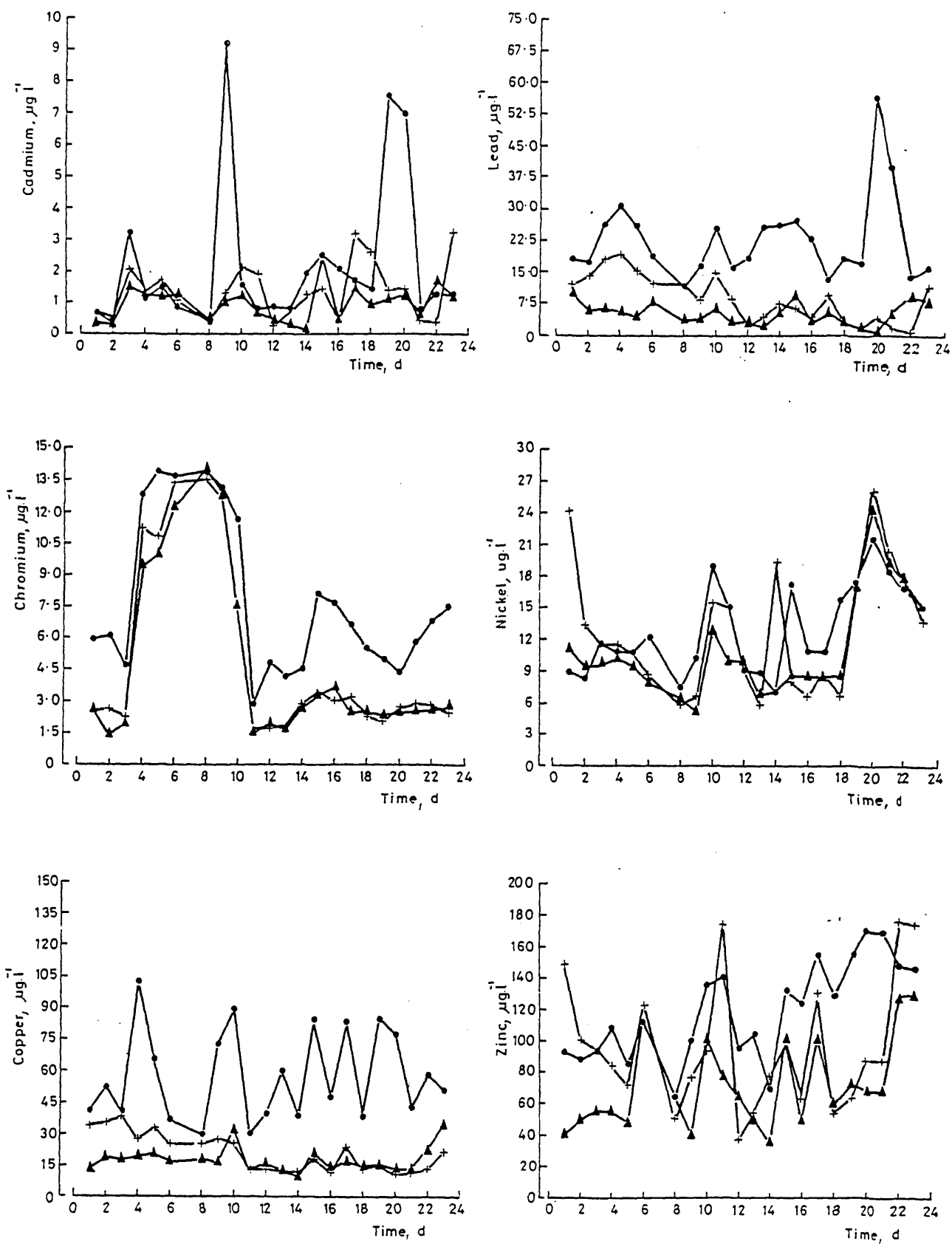


Figure 35 - Heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) in activated sludge pilot plant operated at 9 d sludge age and low metal and low NTA influent concentrations during acclimatization.

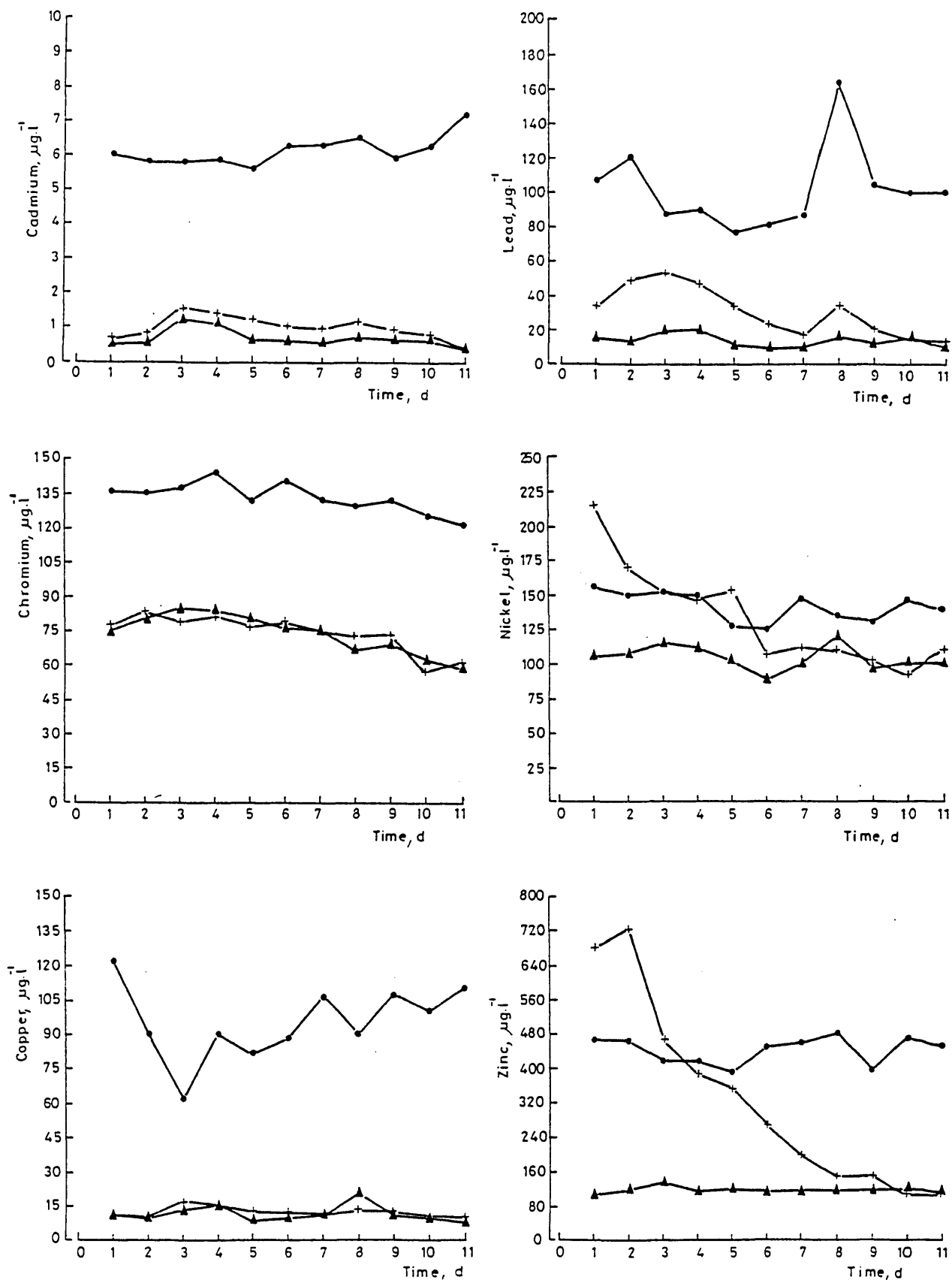


Figure 36 - Heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) in activated sludge pilot plant operated at 9 d sludge age and high metal and low NTA influent concentrations during acclimatization.

Table 39 - Mean values, relative standard deviation, range, percentage removal, mass balance and percentage mobilization for heavy metals concentrations during experiments with low and high heavy metals in the influent, at 9 d sludge age when NTA was added at $7.5 \text{ mg } \ell^{-1}$ during acclimatization.

Metal	System	low heavy metals						high heavy metals					
		Mean $\mu\text{g } \ell^{-1}$	RSD %	Range $\mu\text{g } \ell^{-1}$	Removal %	Mass %	Mobilization %	Mean $\mu\text{g } \ell^{-1}$	RSD %	Range $\mu\text{g } \ell^{-1}$	Removal %	Mass %	Mobilization %
Cadmium	Influent	1.85	131	0.36-9.20	-	-		6.21	7.9	5.60-7.21	-	-	
	Effluent Control	0.88*	47	0.29-1.48	52	156	17	0.64*	45	0.11-1.22	90	133	5
	Effluent Test	1.21*	54	0.24-2.04	35	123		0.91*	48	0.11-1.54	85	112	
Chromium	Influent	9.69	47	2.87-16.2	-	-		131	6.4	113- 144	-	-	
	Effluent Control	6.85	71	1.42-14.1	29	93	4	71.8	12	58.5-85.0	45	106	1
	Effluent Test	7.25	67	1.73-13.4	25	85		70.3	12	57.2-81.3	46	96	
Copper	Influent	54.5	43	29.6- 102	-	-		95.2	12	67.8- 110	-	-	
	Effluent Control	18.3*	26	13.2-20.9	66	92	16	11.2	37	5.60-16.6	88	118	1
	Effluent Test	27.1*	29	13.2-38.3	50	73		12.0*	29	5.57-18.3	87	96	
Lead	Influent	20.4	27	11.5-30.7	-	-		96.9	24	76.8- 165	-	-	
	Effluent Control	5.44*	37	3.20-10.0	73	111	34	12.8*	30	7.37-19.6	87	149	13
	Effluent Test	12.4*	37	2.20-19.2	39	83		24.8*	58	8.09- 53	74	124	
Nickel	Influent	11.2	28	7.48-19.0	-	-		140	6.9	125- 154	-	-	
	Effluent Control	9.28*	22	5.15-12.8	17	93	24	101*	10	86.9- 120	28	111	14
	Effluent Test	12.0*	41	5.83-24.1	(-)7.1	78		120*	17	91.4- 153	14	100	
Zinc	Influent	101	21	64.3- 140	-	-		443	9	392- 530	-	-	
	Effluent Control	64.1*	36	40.0- 113	37	111	32	114*	11	78.3- 135	74	124	23
	Effluent Test	95.5*	40	36.5- 174	5.4	87		219*	57	105- 467	51	105	

* Indicates that the means are statistically different at 5% level of significance

(-) Mobilization from the mixed liquor.

Table 40 - Mean value, relative standard deviation and range for heavy metals concentrations in mixed liquor during experiments with low and high metals in the influent, at 9 d sludge age when NTA was added at $7.5 \text{ mg } \ell^{-1}$ during acclimatization

Metal	Mixed Liquor	low heavy metals			high heavy metals		
		Mean $\mu\text{g } \ell^{-1}$	RSD %	Range $\mu\text{g } \ell^{-1}$	Mean $\mu\text{g } \ell^{-1}$	RSD %	Range $\mu\text{g } \ell^{-1}$
Cadmium	Control	16.1	4.9	15.0-17.1	216	30	87.2- 280
	Test	16.2	14	13.8-20.9	248	20	185- 308
Chromium	Control	191*	36	110- 276	2764*	30	1124-3600
	Test	222*	22	174- 290	3528*	17	2694-4336
Copper	Control	2163*	7.5	1966-2465	3742*	27	1956-5062
	Test	2572*	6.7	2352-2895	4686*	14	3840-5720
Lead	Control	684	9.1	640- 817	2796	31	1374-3724
	Test	648	8.6	565- 731	2882	30	1808-3926
Nickel	Control	148	11	127- 172	1328*	25	762-1726
	Test	126	15	96- 156	1104*	32	776-1584
Zinc	Control	1445*	6.6	1228-1563	13030	33	5462-18956
	Test	1112*	7.7	1005-1219	10928	45	5262-17966

* Indicates that the means are statistically different at 5% level of significance

This could be because of the presence of sodium in the NTA salt used. However this difference does not seem to have any significant effect. The behaviour of phosphates (ortho and total inorganic) were not affected by the presence of NTA.

From the above it may be concluded that the performance of the two plants was similar and any variation in the behaviour of heavy metals could be assumed to be due to the presence of NTA.

Examination of Fig. 35 shows that when NTA was dosed in a system operating with indigenous metal (low metal) zinc, nickel and copper were mobilized during the period when NTA was not completely degraded. As indicated previously (Table 35) the acclimatization phase in this experiment was 12 d. It is evident from Fig. 35 that lead concentrations in the effluent test plant were always higher than the control during these 12 d. For zinc and nickel the mobilization was very high at the beginning of the experiment, but as biodegradation proceeded the degree of mobilization was substantially reduced. This suggests that NTA-zinc and NTA-nickel complexes were formed proportionally to the NTA concentration in the mixed liquor. Copper behaved in a similar manner to lead. However by day 10 of the experiment when the concentration of NTA was 0.6 mg l^{-1} copper ceased to be mobilized. In the case of chromium a high influent concentration was observed during the fourth day of the experiment and persisted until the ninth day when the influent concentration of this metal returned to values within its normal range. During this peak the removal of chromium was reduced and mobilization of this metal in the test plant was observed. This suggests that during the peak in concentration different species of chromium were present with a greater preference for NTA than for the natural ligands in sewage or it may have been the consequence of the elevated influent concentration. For cadmium it was difficult to see any effect on its removal (Fig. 35). Therefore a "t" test was applied to pairs of effluent metal concentrations determined in samples collected during the 12 h since the addition started. The results for the experiment with low metal influent concentrations presented in Table 39 showed that cadmium concentrations in the effluent test were significantly different from the control which suggests that cadmium was mobilized during the acclimatization period. However for chromium no significant

difference was found. Copper, lead, nickel and zinc concentrations in the effluent test and control were significantly different; from Table 39 it can be seen that the removal of these metals was lower in the test plant as well as the removal of cadmium. Chromium appeared to be the only metal not affected by the presence of NTA.

The mass balances in Table 39 were calculated based on the average concentrations of metals in the influent, effluent and mixed liquor. Since average values were used to calculate the mass balance no account in the variation (accumulation or mobilization) of metals in the mixed liquor during the experiment was taken. In this case mass balances were expressed as a percentage of the incoming metal related to outgoing metal in the system as follows:

$$\text{Mass Balance (\%)} = \frac{Q \times C_i \times 24}{Q \times C_e \times 24 + V_w \times C_m} \times 100$$

where

Q = flow to the plant, $\ell \text{ h}^{-1}$

C_i = average metal concentration in influent, $\mu\text{g } \ell^{-1}$

C_e = average metal concentration in effluent, $\mu\text{g } \ell^{-1}$

C_m = average metal concentration in mixed liquor, $\mu\text{g } \ell^{-1}$

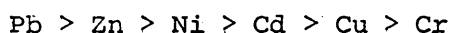
V_w = volume of mixed liquor wasted every day, $\ell \text{ d}^{-1}$

This simplification which ignores accumulation and mobilization induces an error resulting in mass balances for test plant always being lower than mass balances in control. During the period of study in the absence of NTA the mixed liquor functioned as a reservoir for metals. If the amount of metal retained in the mixed liquor was taken into account it would increase the denominator in the formula for calculating the balance and the results would be lower than those found. If the metals mobilized from the mixed liquor by NTA in the test plant were taken into account then this factor would increase the numerator in the formula and the percentage would be higher than it was found to be.

Nevertheless the results obtained show a poor balance for cadmium which can be explained by the nature of the occurrence of this metal in the sewage, that is as peaks of short duration. For the rest of the

metals the values for balances are in the range acceptable for this type of experiment (78-111%).

Data in Table 40 for results from the experiment with indigeneous metal concentrations in the influent (low metal) indicate that the concentrations of lead, nickel and zinc in the mixed liquor were lower in the test plant. This was expected since these metals were mobilized during the acclimatization of NTA. However, cadmium, chromium and copper presented higher concentrations in the mixed liquor treated with NTA. Probably the NTA complexes of these metals were adsorbed onto the flocs and because they are more difficult to degrade the concentration of these metals in the mixed liquor were increased. As the influent metal concentration varied according to the metal it is difficult to identify which metal was most affected by the presence of NTA. Using the percentage mobilization (percentage removal in control - percentage removal in test) which are included in Table 39 it is possible to rank the metals according to the effect of $7.5 \text{ mg } \ell^{-1}$ of NTA on their removal during the total period of this experiment with indigeneous metal, as follows:



During experiments at high metal concentraions the performance of the two pilot plants were similar as can be seen from Table 38. No significant differences were found when comparing the parameters from the two plants at a 5% level of significance. Although the SVI values (295 mL g^{-1} for control and 286 mL g^{-1} for test) which were high compared with the recommended values ($<100 \text{ mL g}^{-1}$), the settleability of the mixed liquor was good resulting in low effluent suspended solids in both plants ($8.5 \text{ mg } \ell^{-1}$ for control and $5.8 \text{ mg } \ell^{-1}$ for test). The two plants did not nitrify very well during the experiment which can be seen from the high values for ammonia ($15 \text{ mg } \ell^{-1}$ as N) found in both plants (Table 38). However COD removal was 77% in the control plant and 81% in the test plant indicating normal functioning of the plant. During this experiment pH values were not affected by the presence of NTA probably because of the buffer capacity of the settled sewage. The behaviour of phosphates in both plants were similar, as observed in the previous experiment, which suggests that NTA does not affect phosphorus removal in the activated sludge process.

Since the operational parameters in both plants were similar it is possible to compare the behaviour of the heavy metals during the acclimatization period when NTA was added at $7.5 \text{ mg } \ell^{-1}$. In Fig. 36 the results from metal analysis of influent and effluents from the pilot plant are plotted. It is evident from Fig. 36 that cadmium, lead, nickel and zinc were mobilized in the presence of NTA. Chromium and copper seem to be unaffected by NTA which was confirmed by the "t" test in which no significant differences were found when comparing effluent concentrations of these metals in the two plants. In this experiment the time required for complete biodegradation of NTA was 10 d, as can be seen in Fig. 37, which is coincident with the period during which lead concentrations were higher in the test plant effluent. Zinc and nickel exhibited mobilization into the effluent, with effluent concentrations in excess of the influent concentrations indicating removal of this metal from the mixed liquor.

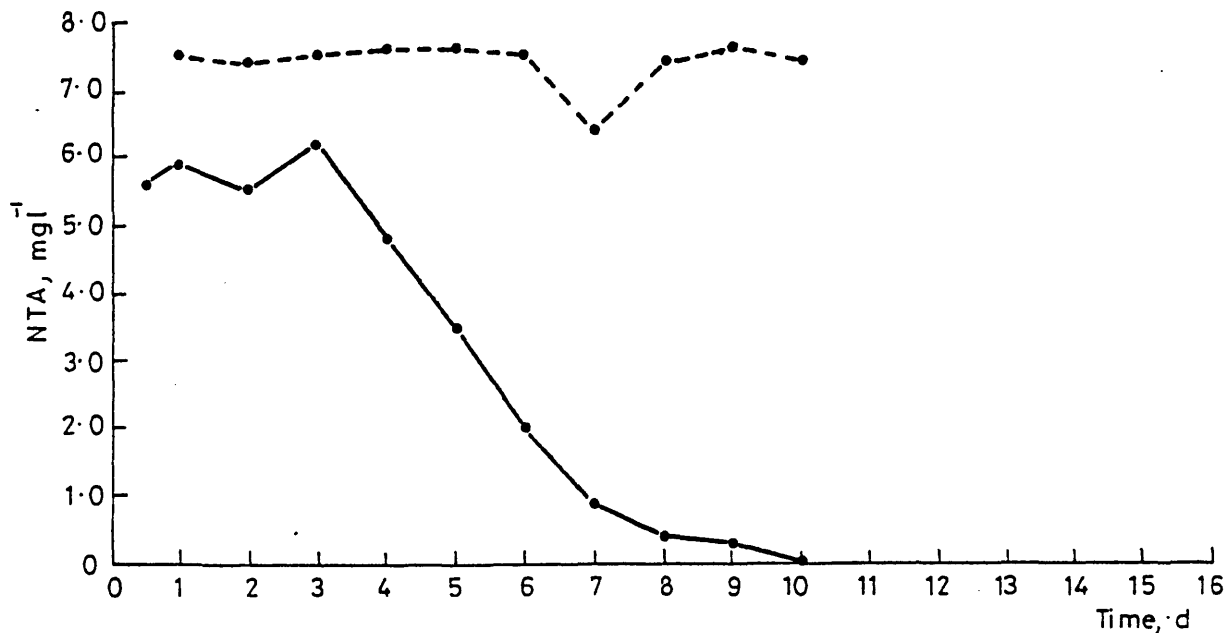


Figure 37 - NTA concentrations in influent (---) and effluent (—) in the activated sludge pilot plant at 9 d sludge age and high metals in the influent when NTA was dosed at $7.5 \text{ mg } \ell^{-1}$ during acclimatization.

It is evident from Table 39 that in this experiment with high influent metal concentrations cadmium, lead, nickel and zinc were substantially mobilized resulting in lower percentage removal in the test plant than in the control. Results from the mass balances in Table 39 indicate the same trend with test plant results lower than the control, nevertheless the mass balances are within the acceptable range ($\pm 20\%$) except for cadmium and lead. For these two metals the occurrence of high peaks of short duration in the influent concentrations have resulted in poor mass balances.

The mobilization of nickel and zinc from the mixed liquor results in a reduction in the concentration of these metals in the mixed liquors which is confirmed by the results presented in Table 40 for the experiment at high influent metal concentrations. However only in the case of nickel a significant difference was found, Chromium and copper concentrations in the mixed liquor from the test plant were higher than the control which suggests an accumulation of these metals in the floc during the early stages of NTA addition. As the concentration of these metals in the effluents from control and test are similar (Fig. 36, Table 39) it would appear that the NTA complex of these metals are adsorbed by the floc and because they are more difficult to biodegrade they stay in the floc increasing the concentration of chromium and copper in the mixed liquor. However, the ability of the floc to remove chromium and copper was not affected by the presence of NTA. Concentrations of cadmium and lead in the mixed liquor from the test plant were higher than the control although this difference was not statistically significant.

Using the percentage mobilizations from Table 39, in the experiment at high influent metal concentration it is possible to rank those metals which were significantly affected when NTA was added at $7.5 \text{ mg } \ell^{-1}$ in the following order:

$$\text{Zn} > \text{Ni} > \text{Pb} > \text{Cd} > \text{Cr, Cu}$$

It is not reasonable to assume that these two experiments at low and high heavy metal influent concentrations were directly comparable since the sewage characteristics were not constant from one experiment to the other, however some conclusions can be drawn with regard to the

presence of metals and NTA. Both zinc and nickel were mobilized from the mixed liquor and their removal was proportional to the effluent NTA concentrations, the concentrations of zinc and nickel in the effluent (Figs 35 and 36) parallel that of NTA (Figs 32b and 37) which suggests that the NTA concentration is important in dictating the behaviour of these two metals in the presence of NTA. At high influent metal concentration when zinc was mostly in a soluble form its mobilization was controlled more by the NTA concentration than by any natural ligands present in the sewage. To a lesser extent the same appears to apply to nickel. Lead was continuously removed in the presence of NTA and the pattern for lead in the effluent test plant exhibited an increase with maximum values during the third and fourth day after the NTA was added which suggests that zinc and nickel compete with lead to form complexes with NTA. Probably the same mechanism could explain the behaviour of cadmium during this experiment. The increase in metal concentrations in the system probably reduced the chance for the formation of large quantities of the NTA-copper complex which explains the failure to mobilize this metal during experiment at high metal concentrations.

4.11 Effect of shock loading ("wash day" simulation) on the biodegradation of NTA at different sludge ages, NTA influent concentrations and heavy metal influent concentrations

A series of experiments was designed to study the response of the activated sludge process to a shock loading due to an increase in the NTA influent concentration. This corresponded to the simulation of a "wash day" when a significant increase in the concentration of a detergent builder in the raw sewage would be expected. That such an increase occurs was confirmed during the experiments reported in sections 4.5 and 4.6 when total inorganic and polyphosphates were monitored in the raw sewage. The results found were plotted and are presented in Fig 44 and 45, (Appendix V). The mean of all the maximum values observed for polyphosphates in the influent was calculated, assuming that the concentration of polyphosphate was equal to the difference between total inorganic phosphate and orthophosphate, and it was found to be 2.6 times the value of the average concentration of polyphosphates. To assess the time of the day that the peak in polyphosphates reached the activated sludge pilot plant and to quantify

the duration of the peak a series of phosphate analyses were undertaken in settled sewage samples collected in the influent of the pilot plant at two-hourly intervals over a period of two days from 21:00 h on Sunday to 17:00 h on Tuesday. The diurnal variation in polyphosphate concentrations is illustrated in Fig. 38. It can be seen that the peak concentration for polyphosphates was reached at 17:00 h on the Monday. A second and lower peak

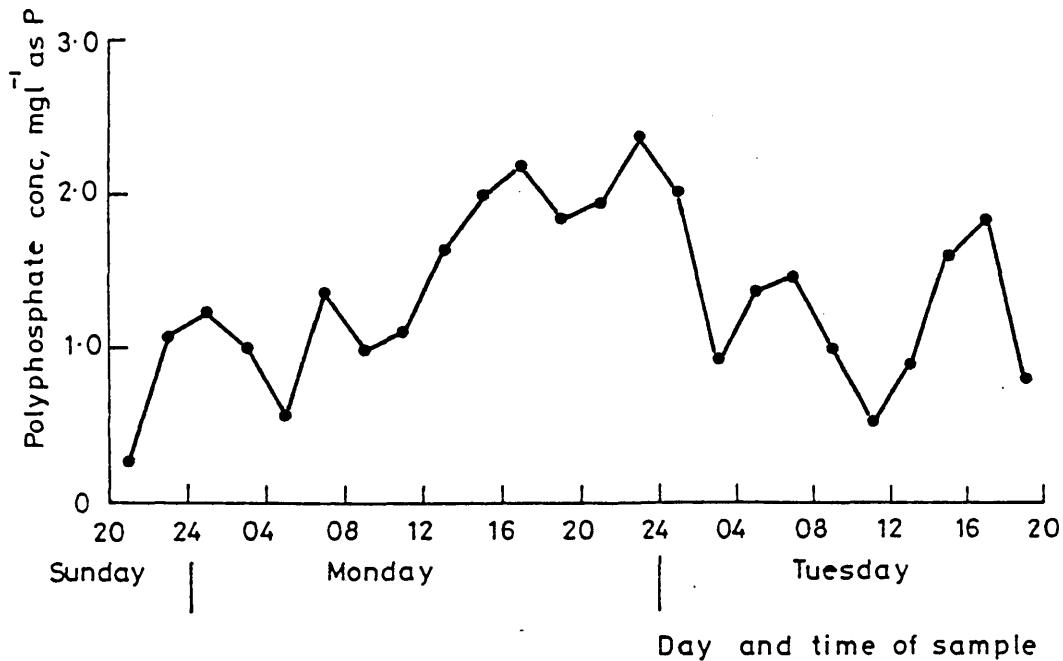


Figure 38 - Diurnal variation of filtered influent polyphosphate concentrations to the activated sludge pilot plant.

occurred at 17:00 h on the Tuesday. When the detention time of the waste water in the sewers and primary sedimentation tanks is considered, a peak phosphate concentration at the activated sludge pilot plant at 17:00 h represents a mid-morning discharge into the sewer, this is probably representative of the laundering patterns within this area. From Fig. 38 it would appear that the duration of the peak was 10 h.

During the experiments reported in this section the pilot plant was fed with settled sewage from Hogsmill Valley Sewage Treatment Works with or without metal addition and NTA was added at 7.5 and

15 mg ℓ^{-1} . The experimental programme was as described in section 3.2.2. After the acclimatization to NTA the plant was operated for a period normally equal to the sludge age and the operational parameters were monitored and controlled. When the performance of the two plants were similar as indicated by the similarity between MLVSS values and effluent SS and COD concentrations and when the effluent of the test contained only low concentrations of NTA, the wash day simulation was carried out. The NTA in the influent was increased to double its original value and this new concentration was maintained until effluent concentrations returned to their original values. During the wash day simulation the concentrations of NTA in the effluent were monitored more frequently during the first 15 h since the chloride tracer test (section 4.9) had indicated that any change in the influent concentration to the system would take 12 h to achieve stable effluent concentration.

4.11.1 Effect of shock load of NTA on its biodegradation at different sludge ages in the activated sludge process at low metal and low NTA influent concentrations.

Three sludge ages (4, 9 and 12 d) were selected to study the influence of shock loading on the biodegradation of NTA at low metal influent concentrations when NTA was added at 7.5 mg ℓ^{-1} (Experiments I, II and III, section 3.2.2). NTA effluent concentrations were analysed during the "wash day" simulation and the results are presented in Figs. 39a, 39b and 39c. When the plant was operating at 4 d sludge age (Fig. 39a), 7 h after the NTA influent concentration was increased from 7.5 to 15 mg ℓ^{-1} , the effluent concentration had increased to 2.0 mg ℓ^{-1} corresponding to a removal efficiency of 73%. The removal efficiency increased progressively to 98% during the 24 h following the increase in the influent concentration and this removal efficiency was sustained for the remainder of the experiment. At 9 d sludge age (Fig. 39b) when the influent NTA concentration was increased to 15 mg ℓ^{-1} the effluent NTA concentration increased progressively to a maximum of 0.60 mg ℓ^{-1} after 8.5 h and remained at this level for approximately 4 h after which the removal efficiency increased to approaching 100%

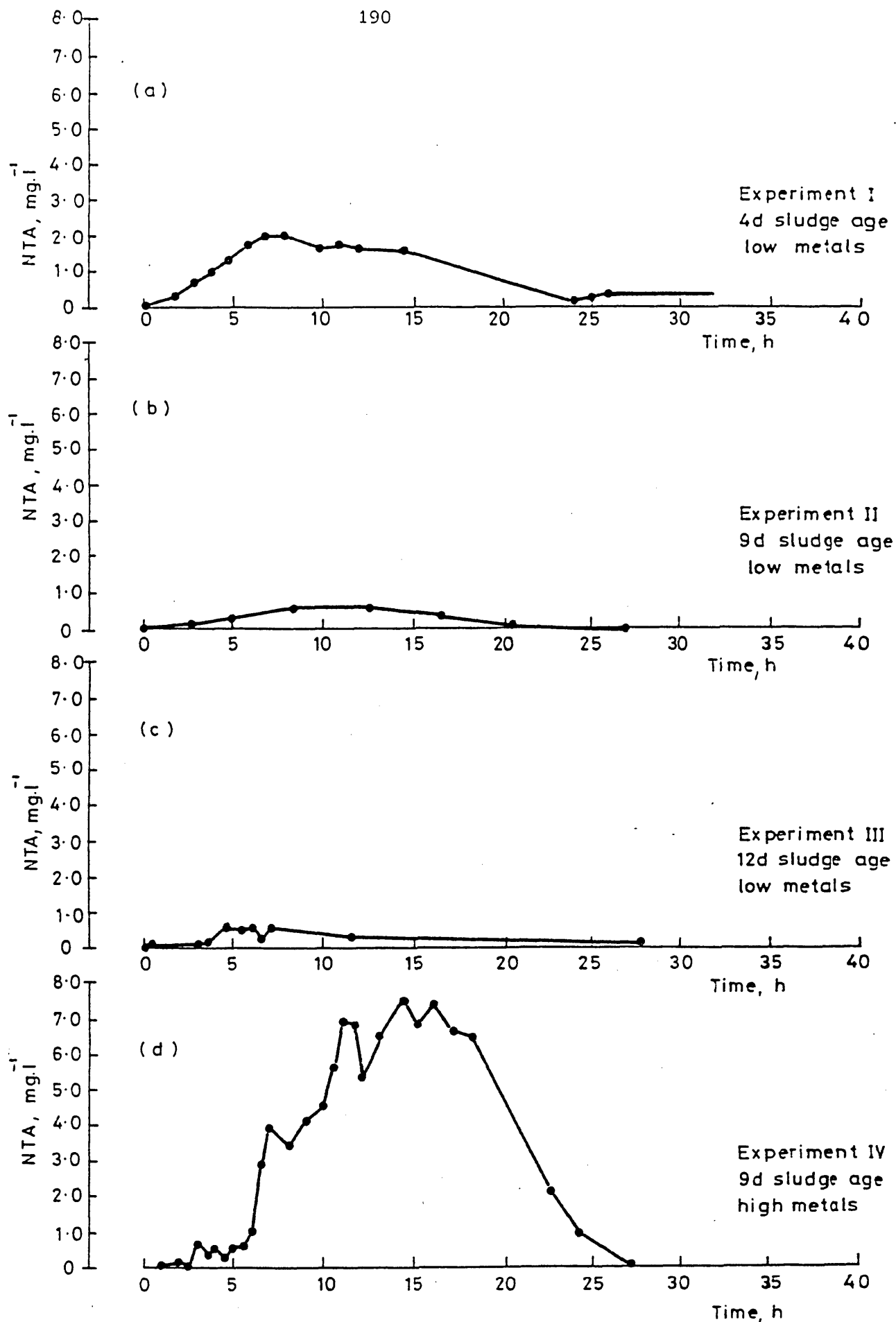


Figure 39 - Variation in effluent NTA concentrations during "wash day" simulation at different metal concentrations when NTA was added at 15 mg l^{-1} .

approximately 27 h after initiation of the wash day simulation. During the experiment at 12 d sludge age (Fig. 39c) when the "wash day" simulation was undertaken an increase in the effluent NTA concentration to $0.60 \text{ mg } \ell^{-1}$ 4 h after the experiment commenced was observed and this persisted for a further 3 h (93% efficiency removal) and then decreased to achieve 99% removal efficiency 27 h after the experiment initiated.

Treatment parameters were also determined during the acclimatization period preceeding the "wash day" simulation. The results are tabulated and presented in Table 48 (Appendix VI) which indicates that both plants were behaving in the same manner before the increase in the influent NTA concentration. Despite the MLSS in the aerator being significantly different from one plant to the other, with $3687 \text{ mg } \ell^{-1}$ in the control and $3385 \text{ mg } \ell^{-1}$ in the test plant, the COD and SS removals were similar indicating that both plants performed in the same manner. Although bulking occurred in both plants during the preceeding acclimatization period for experiments at 4 and 12 d sludge ages the suspended solids in the effluent were in the range normally accepted for this process. Values for mixed liquor and effluent suspended solids are presented in Table 41 for the three experiments in this study .

Table 41 - Mixed liquor and effluent suspended solids concentrations in activated sludge pilot plants operated at different sludge ages and low metal and low NTA influent concentrations during acclimatization period preceeding "wash day" simulation.

Sludge age d	Suspended Solids, $\text{mg } \ell^{-1}$			
	Mixed Liquor		Effluent	
	control	test	control	test
4	1641	1555	10	8.0
9	2934	3230	4.6	3.9
12	3687	3385	17	15

It seems probably that the population size of the NTA degrading bacteria would increase as the sludge age increased (the higher the sludge age the higher the MLSS) and this increase in MLSS would also increase the adsorption capacity of the system, this suggests that the response of the activated sludge process to shock loads of NTA improves as the MLSS concentrations increases due to increase in sludge age and that two mechanisms may be involved, adsorption and biodegradation. This is supported by the observations in Figs. 39a, 39b and 39c when for a low MLSS concentration the system required more time to acclimatize to NTA during the "wash day" simulation.

4.11.2 Effect of shock load of NTA on its biodegradation in the activated sludge process operated at 9`d sludge age with high metal influent concentrations and low NTA influent concentration

At 9 d sludge age when the plant was fed with settled sewage containing high metal concentrations, artificially added (Experiment IV), an increase in NTA influent concentration from 7.5 to 15 mg ℓ^{-1} resulted in a gradual increase in the effluent NTA concentration to 6.9 mg ℓ^{-1} (equivalent to 55% efficiency removal) during the 14 h after the experiment started (Fig. 39d) and remained at this level for 2 h, after which the effluent NTA concentration decreased and complete biodegradation was achieved 27 h after the experiment commenced. From the values for the operational parameters monitored during the acclimatization period preceeding the "wash day" simulation (Appendix VI, Table 49) it can be seen that both plants had the same treatment performance during the peak. Comparing Fig. 39b with Fig. 39d for experiments at the same sludge age and the same NTA influent concentration but with low and high metal influent concentrations respectively and assuming that the operational condition of the plants during these experiments were similar (Appendix VI, Tables 48 and 49) it would appear that the presence of high metal concentrations interfered in the NTA biodegradation mechanism. It is possible that the increase in the influent NTA concentration from 7.5 to 15 mg ℓ^{-1} solubilized metals from the mixed liquor creating a toxic environment for the NTA biodegrading bacteria or inhibiting the mechanism of

biodegradation. Alternatively the formation of less degradable or non degradable complexes may explain these observations. Considering the variability of the sewage matrix from one experiment to another, such as concentration and type of natural ligands, form and concentration of metals, species and population size of the micro-organisms present there appear to be many factors which could potentially influence the peak in NTA effluent concentration during the "wash day" simulation.

4.11.3 Effect of shock load on the biodegradation of NTA in activated sludge process operated at 9d sludge age with low metal and high NTA influent concentrations

To assess the effect of high NTA influent concentration on the biodegradation of NTA an experiment was undertaken (Experiment VIII) when the activated pilot plant was operated at 9 d sludge age, with no metals added to the influent and the NTA concentration was increased from 15 to 30 mg ℓ^{-1} to simulate the "wash day". The NTA concentrations in the effluent were monitored and the results are presented in Fig. 40 d which shows that the response to the shock load was immediate and only a small amount of NTA was detected in the effluent during the first 6 h of the experiment when an average efficiency removal of 99% was observed. The operational parameters for both plants during the acclimatization period preceeding the wash day simulation are presented in Table 49 (Appendix VI) from which it is evident that the two plants exhibited comparable performances. From the results in this experiment it may be concluded that in a completely mixing activated sludge plant when operating with low influent metal concentrations the biodegradation of NTA is not affected by a change in the influent NTA load within the range expected to occur in sewage.

4.11.4 Effect of shock load of NTA on its biodegradation at different sludge ages in the activated sludge process at high metal and high NTA influent concentrations.

Three different sludge ages (4, 9 and 12 d) were used to study the effect of NTA shock loading on the biodegradation of NTA when high NTA

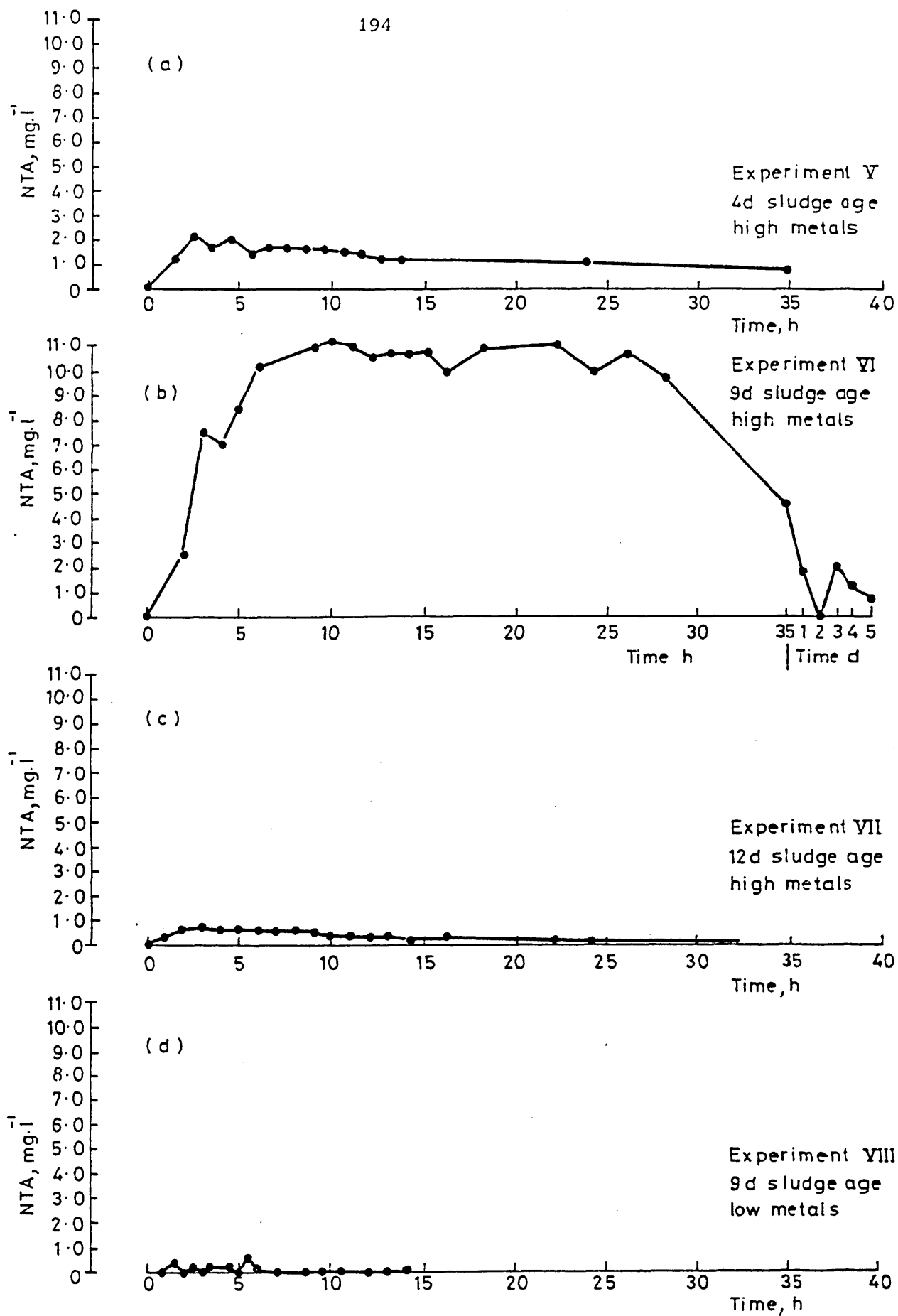


Figure 40 - Variation in effluent NTA concentration during "wash day" simulation at different metal concentrations when NTA was added at 30 mg l^{-1} .

concentrations were dosed into sewage containing high influent metal concentrations (Experiments V, VI and VII, section 3.2.2). Effluent concentrations of NTA were determined in samples collected throughout the experiments after the NTA influent concentration was doubled from 15 to 30 mg ℓ^{-1} and the results are presented in Figs. 40a, 40b and 40c.

At 4 d sludge age when the NTA was increased (Fig. 40a) the NTA effluent concentrations increased rapidly to 1.7 mg ℓ^{-1} during the first 3.5 h and then stabilized for 2 h with a removal efficiency of 89%. After this the effluent NTA concentration decreased to 0.8 mg ℓ^{-1} 45 h after the experiment had commenced when the removal efficiency was 97%. When a shock load was simulated in the pilot plant operating at 9 d sludge age (Fig. 40b) the effluent NTA concentration increased rapidly and a maximum value of 11.1 mg ℓ^{-1} was reached 10 h after the NTA in the influent was doubled (15 to 30 mg ℓ^{-1}). The efficiency of removal at that time was reduced to 62% and stabilized at this value for 14 h after which it began to decrease progressively, until 100% removal was achieved 4 d after the 30 mg ℓ^{-1} NTA dose had commenced. The effect of a shock load in the experiment at 12 d sludge age is presented in Fig. 40 c. The effluent NTA concentrations increased progressively to 0.7 mg ℓ^{-1} during the first 3 h after the influent NTA concentration was doubled and this represented a removal of 98%, this situation persisted for 5 h after which effluent NTA concentration started to decrease and 24 h after the experiment commenced 99% removal was achieved, this persisted for the remainder of the experiment.

Operational parameters were monitored during the acclimatization period preceeding the "wash day" simulation and the mean values are presented in Table 50 (Appendix VI) from which it is evident that the effluent quality from both plants was similar. As in the experiment at low influent metal concentrations there was a gradual increase in the MLSS concentration as the sludge age increased. In order to permit comparison between the three experiments the average MLSS and effluent suspended solids concentrations are presented in Table 42.

Considering the MLSS concentration during these three experiments (Table 42) a rapid response to the shock load was expected as the sludge age increased. The experiments at 4 and 12 d sludge ages (Figs. 40a and 40c) generally conform to this trend. However at 9 d sludge age

Table 42 - Mixed liquor and effluent suspended solids concentrations in activated sludge pilot plants operated at different sludge ages and high metal and high NTA influent concentrations during acclimatization period preceeding "wash day" simulation

Sludge age d	Suspended solids, mg ℓ^{-1}			
	Mixed liquor		Effluent	
	Control	test	Control	test
4	2182	2427	3.0	4.8
9	2640	2964	13	15
12	3742	3822	13	10

a significant increase in the effluent NTA concentration was observed. The presence of high influent metal concentrations at 9 d sludge age seems to be responsible for this behaviour since at this sludge age but at low influent metal concentrations no adverse effect was found (section 4.11.3) when high NTA concentration was added. As the metal influent concentration in this series of experiments was high an adverse effect in the NTA biodegradation at 4 and 12 d sludge age was also expected, since this did not occur it is possible that sludge age in conjunction with high influent metal concentrations may interfere in the biodegradation of NTA. However, the possibility that other factors may be responsible cannot be excluded. The diverse characteristics of the sewage and the possibility that different species of NTA biodegrading bacteria may be present could be important as well as the degree of metal accumulation by the mixed liquor.

4.12 The behaviour of heavy metals during NTA shock loading in the activated sludge process at different sludge ages NTA influent concentrations and heavy metal influent concentrations

To evaluate the behaviour of the heavy metals in the activated sludge process during the NTA shock loading grab samples were collected

throughout the "wash day" simulation and heavy metal determinations undertaken, these are reported in section 4.11. Normally the samples were collected every hour during first 15 h and from then on with less frequency until the NTA effluent concentration returned to its original value. This period of 15 h was chosen since the chloride tracer test (section 4.9) indicated that 12 h was the time required for the system to achieve a stable effluent concentration after any change in the influent concentration. Metal removals were calculated during the 15 h of each experiment to allow comparison of the control and test plant performance and to facilitate calculation of the percentage mobilization. Since the period of observation was short no attempt was made to compare metal removal between experiments.

4.12.1 Effect of NTA shock loading on heavy metal removals in activated sludge process operated at different sludge ages and low influent metal and NTA concentrations

Three sludge ages (4, 9 and 12 d) were studied as reported in section 4.11.1. Grab samples were collected and analysis of their metal content undertaken, the mean values were calculated for influent and effluent metal concentrations, these results are tabulated in Table 43, in addition the percentage removal and percentage mobilization for those metals significantly mobilized are also included. During the experiment at 4 d sludge age when the "wash day" simulation was undertaken the effluent NTA concentration reached 2 mg l^{-1} , the concentrations of copper, lead, nickel and zinc were significantly different in the effluents of the control and test pilot plant indicating that NTA mobilized these metals and as a consequence a decrease in their removal was observed. Zinc was the metal most affected followed by lead, copper and nickel. Chromium was significantly affected as well, but in the opposite manner to the other metals its removal increased in the test plant which suggests that other metals were removed from the activated sludge floc due to NTA, thus leaving sites which were occupied by chromium. Cadmium was not affected by the presence of NTA. When the influent NTA concentration

Table 43 - Mean values for influent and effluent heavy metal concentrations, percentage removal (% R) and percentage mobilization (%M) during experiments at different sludge ages and different NTA influent concentrations and low influent metal concentrations.

Metal	System	NTA added at 15 mg ℓ^{-1}									NTA added at 30 mg ℓ^{-1}		
		4 d sludge age			9 d sludge age			12 d sludge age			9 d sludge age		
		conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M
Cadmium	Influent	0.40	-		1.89			2.91	-		1.53	-	
	Effluent Control	0.11	73	NA	1.57	17	NA	1.47	49	NA	1.13	26	NA
	Effluent Test	0.09	78		1.67	11		1.34	54		1.26	18	
Chromium	Influent	67.5	-		3.95	-		5.00	-		7.64	-	
	Effluent Control	63.1*	7	-14	1.17	70	NA	2.28	54	NA	3.60	53	NA
	Effluent Test	53.2*	21		1.15	71		2.39	52		3.29	57	
Copper	Influent	43.6	-		44.6	-		67.7	-		45.5	-	
	Effluent Control	4.67*	89	6	14.8	67	NA	10.9	84	NA	8.35	82	NA
	Effluent Test	7.29*	83		13.8	69		13.7	80		7.75	85	
Lead	Influent	19.5	-		17.3	-		18.7	-		18.2	-	
	Effluent Control	5.24*	73	9	3.77	78	NA	6.81	64	NA	11.2	38	NA
	Effluent Test	7.11*	64		4.37	75		6.57	65		11.4	27	
Nickel	Influent	31.9	-		21.5	-		11.4	-		51.8	-	
	Effluent Control	21.3*	33	5	10.5	51	NA	8.88	23	NA	50.0	3.5	NA
	Effluent Test	22.8*	28		9.78	55		8.82	23		50.3	2.9	
Zinc	Influent	92.0	-		90.5	-		95.8	-		104	-	
	Effluent Control	39.5*	57	17	56.5*	38	19	54.0	44	NA	54.1	48	NA
	Effluent Test	55.2*	40		73.7*	19		48.6	49		45.5	56	

* indicates that the means are statistically different at 5% level of significance

NA - not applicable.

was increased from 7.5 to 15 mg ℓ^{-1} during the "wash day" simulation in the plant operating at 9d sludge age only zinc was significantly influenced by the increase in NTA effluent concentrations from 0 to 0.6 mg ℓ^{-1} as can be seen in Table 43, when zinc removal was reduced from 38 to 19%. During the experiment at 12 d sludge age no effect on metal removal due to NTA shock loading was detected (Table 43), although 0.6 mg ℓ^{-1} of NTA was measured in the effluent.

Since the peak NTA concentration in the effluent during the "wash day" simulation at 4 d sludge age was higher compared with the other sludge ages (section 4.11.1) it was anticipated that metal mobilization would be greatest at this sludge age which is evident from Table 43. It may be concluded that the presence of NTA in the effluent, due to its failure to biodegrade may mobilize metals and this effect is proportional to the amount of NTA released. Heavy metals were not mobilized at 12 d sludge age experiment despite the NTA concentration during the peak being similar to that found in experiment at 9d sludge age (0.6 mg ℓ^{-1}) when zinc was mobilized. It is possible that an increase in sludge age produced activated sludge flocs which were more competitive for metals than NTA.

4.12.2 Effect of NTA influent concentration on heavy metal removal during the "wash day" simulation in activated sludge process operated at 9 d sludge age and low metal influent concentration.

Metal concentrations were monitored in the experiment at 9 d sludge age with low metal and NTA influent concentrations during the "wash day" simulation when the NTA concentration was increased from 15 to 30 mg ℓ^{-1} (section 4.11.3). No heavy metal mobilization was observed during the experiment despite the NTA effluent concentration rising to a maximum of 0.6 mg ℓ^{-1} during the peak (Table 43). A comparison of the results from Table 43 for experiments at the same sludge age suggests that an increase in NTA influent concentration did not affect the metal removal since biodegradation of NTA was not affected. In the case of zinc which was mobilized in the experiment at low NTA influent concentration but not at the high NTA influent concentration, it is probable that differences in the characteristics of the sewage

matrix were responsible for these observations which is confirmed by the different removals for zinc in experiments at 9 d sludge age (Table 43). Lower metal removal could indicate less affinity for the activated sludge floc and possibly more affinity for NTA.

4.12.3 Effect of NTA shock loading on heavy metal removal in the activated sludge process operated at different sludge ages at high influent metal and NTA concentrations

During the experiments reported in section 4.11.4 when the plant was operated at different sludge ages (4, 9 and 12 d) and with high influent metal concentrations the shock load was simulated by the increase in NTA from 15 to 30 mg ℓ^{-1} . Metal concentrations were monitored throughout the experiments and mean values, percentage removal and percentage mobilization were calculated over the 15 h period of study, these are presented in Table 44. When the plant was operated at 4 d sludge age a maximum effluent NTA concentration of 1.7 mg ℓ^{-1} was measured, zinc and nickel were substantially mobilized, cadmium, chromium and lead also were mobilized but to a lesser extent and no significant effect was detected for copper. The effluent nickel concentration in the test plant was higher than the influent concentration which suggests that this metal was mobilized from the mixed liquor during the shock loading. Comparing the percentage mobilization in the experiment at 4 d sludge age in Table 44 the following order reflects the effect of NTA on the metals

$$\text{Zn} > \text{Ni} > \text{Pb} > \text{Cd} > \text{Cr}$$

At 9 d sludge age when the NTA influent concentration was doubled a substantial amount of the additional NTA was not degraded resulting in high concentrations of NTA (11.1 mg ℓ^{-1}) in the effluent as can be seen in Fig. 40b. Metal analysis was undertaken on the samples collected during this experiment and the mean values, percentage removal and percentage mobilization during the first 15 h after the NTA influent was increased were calculated and are presented in Table 44. Influent and effluent metal concentrations during the whole experiment are shown in Fig. 41, these indicate that zinc, nickel, lead and cadmium were substantially mobilized in the presence of NTA. The concentration of zinc

Table 44 - Mean values for influent and effluent heavy metal concentrations, percentage removal (%R) and percentage mobilization (%M) during experiment at different sludge ages and different NTA influent concentrations and high metal influent concentrations.

Metal	System	NTA added at 15 mg ℓ^{-1}									NTA added at 15 mg ℓ^{-1}		
		4 d sludge age			9 d sludge age			12 d sludge age			9 d sludge age		
		conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M	conc $\mu\text{g } \ell^{-1}$	%R	%M
Cadmium	Influent	6.62	-		14.2	-		8.83	-		6.57	-	
	Effluent Control	1.68*	75	3	4.38*	69	26	3.00*	66	-5	0.24	96	NA
	Effluent Test	1.83*	72		8.10*	43		2.56*	71		0.22	97	
Chromium	Influent	86.0	-		100	-		91.4	-		125	-	
	Effluent Control	27.4*	68	2	35.3	35	NA	29.3	68	NA	61.2	51	NA
	Effluent Test	29.6*	66		36.0	36		28.1	69		57.9	54	
Copper	Influent	130	-		172	-		198	-		105	-	
	Effluent Control	16.1	88	NA	26.3	84	NA	15.9	92	NA	6.54	94	NA
	Effluent Test	15.7	87		29.2	83		13.8	93		6.88	93	
Lead	Influent	60.5	-		68.2	-		62.2	-		115	-	
	Effluent Control	11.6*	81	5	13.8*	80	47	7.63	88	NA	8.77*	92	3
	Effluent Test	14.6*	76		45.9*	33		8.21	87		13.1*	89	
Nickel	Influent	80.8	-		147	-		87.6	-		152	-	
	Effluent Control	62.1*	23	26	121*	18	25	70.8*	19	16	93.4*	38	14
	Effluent Test	83.5* (-)	3		157* (-)	7		85.0*	3		127 *	24	
Zinc	Influent	705	-		579	-		665	-		510	-	
	Effluent Control	236*	66	35	339*	41	134	367*	45	18	99*	81	11
	Effluent Test	467*	31		1116*	(-)93		487*	27		151*	70	

* Indicates that the means are statistically different at 5% level of significance.

(-) Mobilization from the mixed liquor

NA - Not applicable.

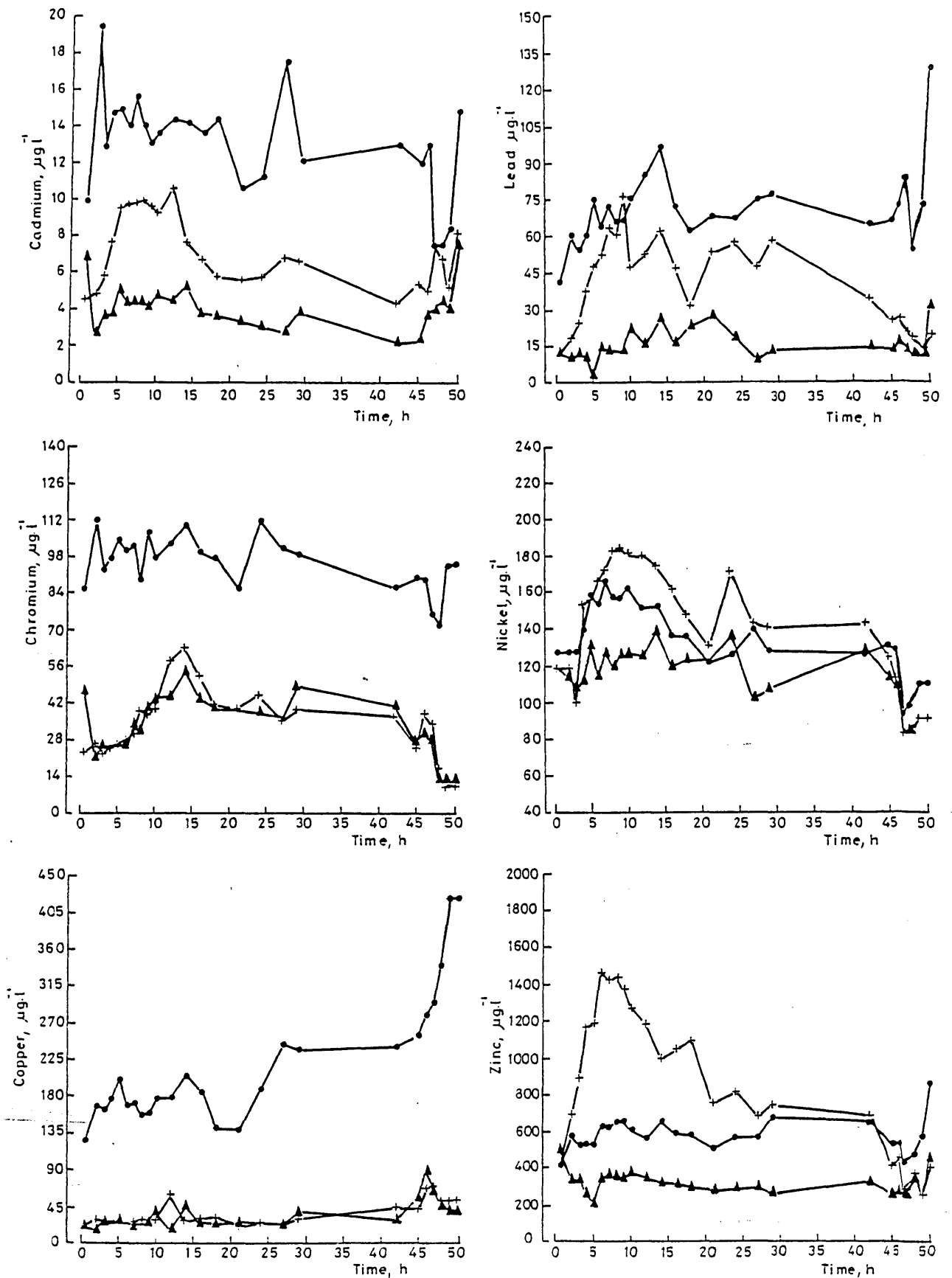


Figure 41 - Heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) in activated sludge pilot plant operated at 9 d sludge age and high metal and high NTA influent concentrations during "wash day" simulation.

and nickel in the effluent increased following the same pattern for the NTA effluent concentration during the wash day simulation Fig. 40 b, which suggests that zinc and nickel mobilization are closely related to the NTA concentration in the mixed liquor. For these metals mobilizations from the mixed liquor were observed since the effluent concentrations were higher than the influent. The mobilization of lead and cadmium exhibited a rapid increase when the experiment started but the concentration of these metals in the effluent was less dependent on the concentration of NTA in the mixed liquor since even very low concentrations of NTA induced their mobilization. Chromium was also mobilized during the period when the NTA concentration in the mixed liquor was elevated (10 - 25 h). The percentage removals for cadmium, lead, nickel and zinc, in Table 44 indicate that during the first 15 h of the experiment these metals were mobilized and it was possible to calculate the percentage mobilization and from them the effect of NTA on metals, which was in the following order



If it is assumed that the difference between the concentrations of metals in the test and in the control pilot plant effluents is equivalent to the concentration of NTA-metal complexes formed then the amount of NTA required to form these complexes may be calculated stoichiometrically since 1 gram atom of metal will be bound by 1 gram mol of NTA. From the results of metal analysis undertaken in samples collected 6 h after the experiment had commenced the quantity of metal mobilized was determined and this corresponded to 183.9×10^{-7} gram atoms, (Table 45)), which will be bound by 3.46 mg of NTA assuming that 1 gram atom of metal will bind 188.1 g of NTA (mol.wt. NTA^{3-}). Comparing this result with $10.1 \text{ mg } \ell^{-1}$ of NTA determined in effluent samples collected at the same time as the metal samples this suggests that other NTA-metal complexes were present in the effluent besides the heavy metal complexes at that time. From this observation it would appear that the mechanism of NTA biodegradation was inhibited and possibly it was not only heavy metal NTA complexes which were being discharged in the effluent but also the normally biodegradable NTA-complexes formed with calcium and magnesium. When the activated sludge pilot plant was operated at 12 d sludge age with high metal

Table 45 - Quantities of cadmium, chromium, lead, nickel and zinc chelated by NTA, 6 h after the commencement of addition, in the effluent of the activated sludge pilot plant operated at a sludge age of 9 d with high influent heavy metal and NTA concentrations.

Metal	Difference conc. effluents test - control $\mu\text{g } \ell^{-1}$	Atomic weight	gram atoms $\times 10^{-7}$
Cadmium	5.4	112	0.5
Chromium	2.3	52	0.4
Lead	38	207	2.0
Nickel	52	59	9.0
Zinc	1116	65	172.0
Total			183.9

influent concentrations during the NTA shock loading the effluent NTA concentrations reached a maximum value of $0.7 \text{ mg } \ell^{-1}$ and as can be seen in Table 44 nickel and zinc were mobilized during the first 15 h after the experiment was initiated. Cadmium removal was improved in the presence of NTA which suggests that the NTA by removing other metals from the mixed liquor created sites for cadmium to be bound.

Comparing the results from these three experiments (Table 44) at different sludge ages some conclusions can be drawn. As the sludge age increases the number of metals affected by the presence of NTA is reduced. Even at high concentrations of NTA in the mixed liquor at 9 d sludge age copper and chromium were not mobilized, nevertheless chromium was mobilized at 4 d sludge age and at a lower NTA concentration in the mixed liquor. This suggests that with increasing in sludge age the affinity of the metals for the biomass also increased and consequently a reduction in the affinity of the metals for NTA, this probably explains the behaviour of cadmium which at 12 d was removed better in the presence of NTA than at 4 d sludge age when it was mobilized by NTA.

This is also applicable to copper which was not mobilized during the experiments and always demonstrated a high removal indicating that copper had a greater affinity for the biomass than for NTA. However, the removal of zinc and nickel was always inferior in the presence of NTA and if the NTA concentration was high (at 9 d sludge age) these metals were mobilized from the mixed liquor. Lead was mobilized in experiments at 4 and 9 d sludge age but not at 12 d sludge age.

4.12.4 Effect of NTA influent concentration on heavy metal removal during the "wash day" simulation in the activated sludge process operated at 9 d sludge age with high metal influent concentration

The increase of the influent NTA concentration from 7.5 to 15 mg ℓ^{-1} during the "wash day" simulation in the plant operating at 9 d sludge age with high metal influent concentrations resulted in a substantial increase in the NTA effluent concentration as reported in section 4.11.2 with a maximum peak of 6.9 mg ℓ^{-1} of NTA in the effluent occurring 14 h after the experiment started (Fig 39 d). Metal concentrations in the effluent were monitored throughout the experiment until low effluent NTA concentrations were detected, this occurred 27 h after the experiment had commenced, the results are plotted in Fig. 42. Mean concentrations of metal in the influent and effluent, percentage removal and percentage of mobilization were calculated for the 15 h after the start of the experiment and the results are presented in Table 44. From Fig. 42 it is evident that zinc, nickel and lead were mobilized during the NTA peak in the "wash day" simulation. This fact was confirmed by the "t" test where significant differences were found between effluent concentrations of those metals in the control and test plant (Table 44). Nickel was mobilized from the mixed liquor which can be seen in Fig. 42 where nickel effluent concentrations in the test plant were higher than the influent concentrations and its mobilization seems to have been related to the concentration of NTA in the mixed liquor since the nickel concentration in the effluent followed the same pattern for NTA during the peak (Fig. 39 d). Zinc and lead to a lesser extent follow the same pattern. Chromium during the peak in NTA effluent concentration which occurred between 10 - 15 h was fixed

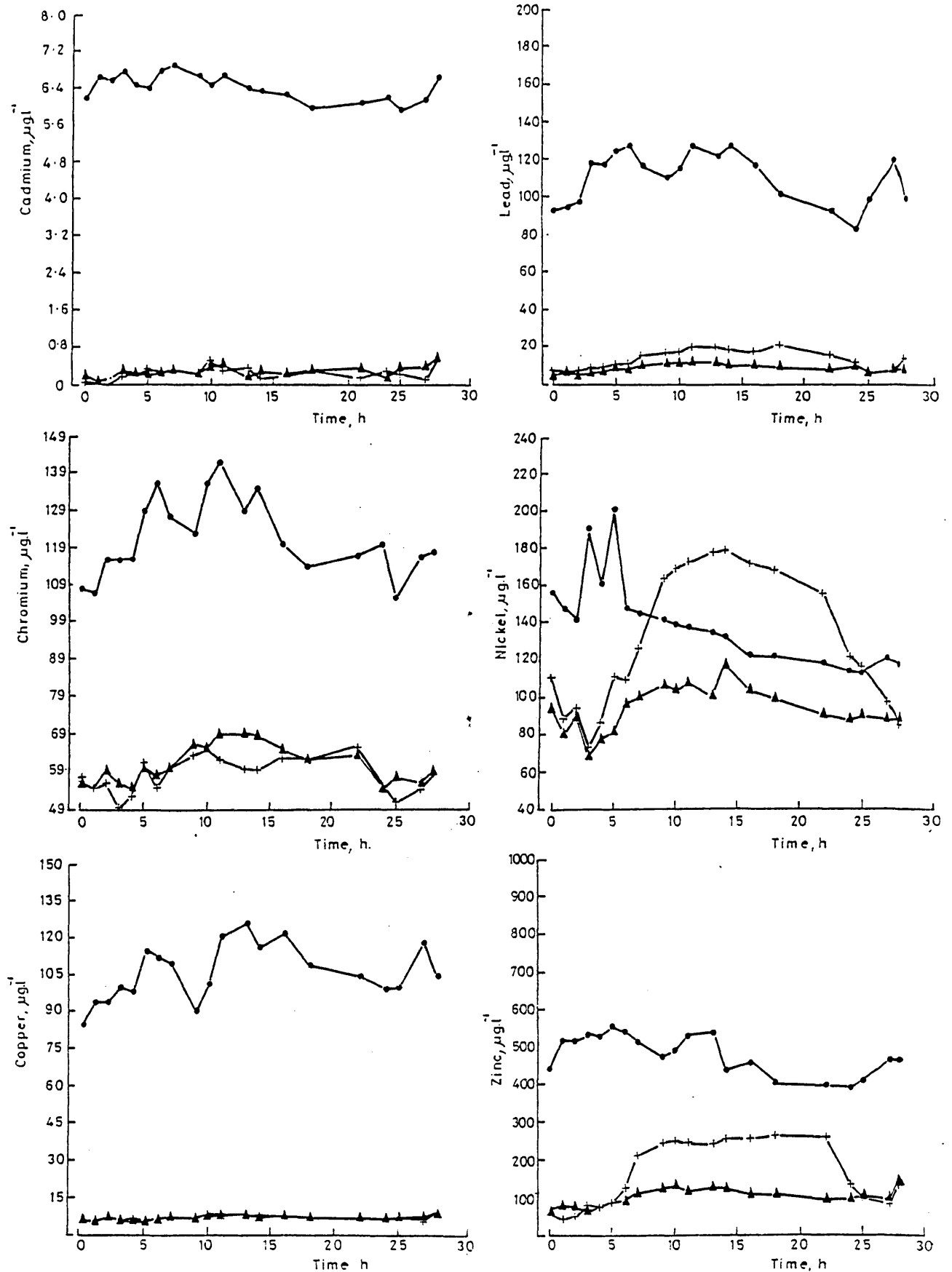


Figure 42 - Heavy metal concentrations in influent (—●—), effluent control (—▲—) and effluent test (—+—) in activated sludge pilot plant operated at 9 d sludge age and high metal and low NTA influent concentrations during "wash day" simulation.

in the mixed liquor since low chromium concentrations were detected in the effluent during this time. Cadmium and copper were not affected by the presence of NTA. From the values of percentage mobilization (Table 44) it is possible to rank metals affected by NTA in the following order



If the same assumption is made as described previously (section 4.12.3) then it is possible to calculate the amount of NTA necessary to complex with the heavy metals mobilized during this experiment and measured in samples collected during the 15 h after the experiment had started, i.e. when the maximum concentration of NTA were detected in the effluent (6.9 mg l^{-1}). Since $8.64 \text{ }\mu\text{g}$ of lead, $61.9 \text{ }\mu\text{g}$ of nickel and $129.7 \text{ }\mu\text{g}$ of zinc per litre of effluent were mobilized, which corresponds to 0.4×10^{-7} , 10.0×10^{-7} and 20.0×10^{-7} gram atom of these metals, respectively, the total of 30.4×10^{-7} mol grams or 0.57 mg of NTA would be required to complex with these metals. Comparing this value with the actual value analysed it is probably that others NTA-metal complexes than those formed with heavy metals are leaving the plant during the NTA peak and that these must include the biodegradable complexes formed with such abundant ions as calcium and magnesium. It would appear therefore that the presence of heavy metals has in some way inhibited the process of biodegradation and that their effect is not solely due to the formation of non-biodegradable complexes since their concentrations are not sufficient to explain the effluent NTA concentrations observed.

Comparing the results for experiments at the same sludge age but with different NTA influent concentrations (Table 44) it is possible to conclude that the increase in NTA concentration in the influent in the presence of high influent metal concentrations resulted in a larger peak of NTA in the effluent and correspondingly more metal was mobilized. There was a difference in the order of magnitude in mobilization from one experiment to the other but always zinc, nickel and lead were mobilized. The difference in this order could be due to the different characteristics of the sewage used on different occasions, the concentration and species of ligands and metals, or the concentration of NTA present in the mixed liquor.

5 DISCUSSION

The dispersal of heavy metals into the environment arising from industrial and domestic wastes is inevitable. Although some controls may be imposed on industrial processes it would be impossible to reduce the concentrations of heavy metals in waste waters to negligible levels because of the contributions from fuel combustion, road run-off and particularly domestic sources, which in some cases may be more significant than industrial sources (Klein et al., 1974). Thus any process which results in the immobilization of heavy metals from waste waters is desirable since their dispersion in the aquatic environment may be reduced and the consequences of heavy metal pollution of surface waters and waters used for aquaculture, irrigation and abstraction of drinking water may be avoided.

Significant quantities of heavy metals from a variety of sources are ultimately transported to sewerage systems. Having reached the sewage treatment process, heavy metals may pass through the process to be discharged to receiving waters in the effluent, or they may be concentrated in the sludges produced. Despite the fact that the ultimate disposal of sewage sludges may potentially result in health hazards due to contamination of agricultural soil or pollution of groundwaters, it may be considered more desirable to concentrate heavy metals in the sludges since their final return to the environment may be more carefully controlled than if they were discharged in sewage effluents.

The removal of heavy metals in sewage treatment processes has long been recognised (Stones, 1955; 1958; 1959a; 1959b; 1960) and several studies have shown typical removal efficiencies of the order of 50% - 80%. However, heavy metal removal appears to be only a beneficial side-effect to the main purpose of sewage treatment processes, and the factors controlling the fairly wide variations in removal efficiency are not fully understood.

The efficiency of sewage treatment processes in removing heavy metals depends on two main factors, namely their existence as settleable particulate forms in the sewage and the conversion of soluble and non-settleable forms to settleable forms within the

process. Thus the purely physical processes involved would be expected to remove very little soluble metal, and the efficiency of removal would be related to the ratio of soluble to particulate forms of each metal in the influent. Oliver and Cosgrove (1974) found that the apparent removal efficiencies of dissolved metals in primary sedimentation were all less than 1% for copper, lead, nickel and zinc.

The heavy metal removal efficiencies in the primary sedimentation pilot plant varied considerably, not only in terms of the effects of hydraulic loading on the process but also with respect to the different methods used to calculate removals. These variations were almost certainly due to the manner of heavy metal input to the process. It appeared that metal input was not a continuous process, since a comparison of the influent heavy metal concentration with the flows to the Hogsmill Valley Works, which were determined every 3 h, indicate that concentrations of cadmium, copper, lead and zinc would increase by a factor of 2 or 3, and then returned to their initial levels in period as short as 12 h. During experiments at a full scale sewage treatment works, when samples were collected hourly, Oliver and Cosgrove (1974) found that similar variations in influent heavy metal concentrations sometimes involving up to tenfold changes, could occur during periods of 6 h. This suggests that each of the methods used to calculate heavy metal removals would be subject to some error due to the limitations imposed by the methods of sampling. The extent of these errors in each case is indicated by the mass balances, which show that in six out of eight occasions the mass balances for lead were less than 70%, demonstrating that the sampling regime failed to obtain representative estimates of the lead concentrations, possibly because this metal entered the Works in the form of slugs lasting for a discrete period of time (Oliver and Cosgrove, 1974). Similar errors in constructing mass balances were obtained by Lewin and Rowell (1973). Balances for cadmium, copper and lead of 69%, 124% and 137% respectively were attributed to limitations in the sampling technique and the need to make observations over a long period of time. Balances calculated from the data of Lester *et al.*, (1979) and Stoveland *et al.*, (1979e) for four 24 h periods at a full-

scale treatment works indicated that nickel and chromium behaved in a similar fashion to lead in this study, having mass balances of 46% and 67% respectively. However, little evidence was obtained to suggest that variations in concentration influenced heavy metal removal.

The variations in heavy metal concentrations in the raw sewage during the primary sedimentation studies reported here were fairly large, ranging from threefold variations in the concentration of zinc, to sixfold variations in the concentrations of cadmium. However, despite these variations, the variations in percentage removals of heavy metals were much less, and moreover, those variations in removal which did occur did not appear to be related to the influent heavy metal concentrations. In contrast, heavy metal removals from the settled sewage in the activated sludge pilot plant showed that atypically low removals of cadmium and chromium coincided with abnormally high concentrations of these metals in the influent. These poor removals may have resulted from a failure of the biomass to adsorb the larger concentrations of cadmium and chromium. It has been proposed that activated sludge has a fixed capacity for the uptake of heavy metals (Esmond and Petrusek, 1974; Kanz *et al.*, 1976), such that if an extra load were introduced, the number of available adsorption sites could be significantly reduced (Forster, 1976). A decline in the capacity of activated sludge to adsorb heavy metals with increasing concentrations has been observed by Sterritt *et al.*, (1981), although this was not considered to be due to saturation of available sites but rather the establishment of a logarithmic relationship between soluble and adsorbed metals.

Although there is some evidence to suggest that heavy metal removal in the activated sludge process is inversely related to the influent heavy metal concentration, the removal efficiencies observed in this study when heavy metals were added to the settled sewage were broadly similar to the removals observed when metals were not added. This may suggest that activated sludge has the capacity to remove significant concentrations of heavy metals under steady state conditions, but that transient shock loads would produce a temporary decline in removal efficiency.

The heavy metal removal efficiencies observed in this study are difficult to compare quantitatively with those found by other workers since they vary considerably according to the plant operating parameters. Such variations were reflected in this study by lead in the primary sedimentation, whose removals ranged from 4% to 65% under different flow conditions, and cadmium in the activated sludge pilot plant whose removals ranged from 8% to 80%. Generally, however, typical removals of cadmium, chromium, copper, lead and zinc in primary sedimentation during dry weather flow conditions were in the range 30 - 50%. while nickel removals were slightly lower, which is in agreement with studies reported on full-scale plants by Stones (1955, 1958, 1959a, 1959b, 1960), Oliver and Cosgrove (1974) and Roberts *et al.*, (1977). Typical removals of cadmium, chromium, copper and lead in the activated sludge pilot plant were greater than 50%. zinc removals were slightly lower and nickel removals were less than 40%. These values are also in agreement with previous studies (Oliver and Cosgrove, 1974; Chen *et al.*, 1974; Brown *et al.*, 1973). The fairly wide variations in heavy metal removal in the primary sedimentation and activated sludge pilot plants suggest that the operating parameters for these processes can significantly influence heavy metal removals. During primary sedimentation, the removals of cadmium, chromium, copper and zinc were adversely affected by increasing the flow by a factor of three and by operating the plant under variable flow conditions. However, the suspended solids removals were not affected by increasing the flow, although the poorest removals of suspended solids occurred during variable flow conditions. Tebbutt and Christoulas (1975) and White and Allos (1976) found that the suspended solids removal in primary sedimentation was influenced to a greater extent by influent suspended solids concentration than by overflow rate. Thus, despite the fact only heavy metals in particulate forms are removed in primary sedimentation (Oliver and Cosgrove, 1974), the removal of heavy metals in this study with the exception of lead, did not appear to be related to the removal of suspended solids. This suggests that the distribution of heavy metals in particulate form was dissimilar to the distribution of the total suspended solids. Some evidence for this suggestion was obtained from correlations of heavy

metal concentrations in the primary sludge with the volatile and non-volatile solids fractions. These indicate that cadmium, chromium, copper, lead and zinc were probably largely associated with inorganic particulates, whereas the majority of primary sludge solids appeared to be organic. In contrast, the nickel in primary sludge appeared to be associated mainly with the organic fraction, except when the flow to the pilot plant was increased by a factor of three. This may indicate that the particulate organo-nickel associations in primary sludge were only poorly settled at higher flow of raw sewage. The heavy metal removals calculated from metal concentrations in 3 hourly samples of raw and settled sewage and from composite samples of raw sewage and primary sludge, which demonstrate reduced removal at higher flows, may suggest that particulate forms of heavy metals belong to a class of particles whose settleability is sensitive to flow rate. If this is the case then optimisation of metal removal may involve operation of the primary sedimentation process with relatively low, constant flow rates.

In the activated sludge pilot plant, when metals were added to the system there appeared to be a trend towards increased removals at longer sludge ages in the cases of chromium, nickel and lead. This trend was paralleled by the accumulation of all the heavy metals by the mixed liquor, which also increased with increasing sludge ages. Copper removal appeared to be independent of sludge age, while the maximum removals of cadmium and zinc occurred at the 9d sludge age. The removals of zinc, lead, nickel and chromium from the unspiked settled sewage, when the influent concentrations were much lower, were highest at the 9 d sludge age, as were the maximum accumulations of chromium, copper, nickel and lead. In studies on a laboratory scale activated sludge simulation, Sterritt and Lester (1981) found that the accumulation of several heavy metals by mixed liquor solids increased as the sludge age was increased from 3 d to 12 d, but decreased as the sludge age increased further. However, the maximum removal efficiencies observed did not occur at the same sludge age as maximum accumulation by the biomass. These results indicate that enhanced heavy metal removal may occur at longer sludge ages,

although beyond a certain limit removal efficiency may decline, suggesting that factors other than sludge age may influence metal removal. Although the removal of heavy metals may be determined to some extent by the operational control of the activated sludge process, removal efficiency may also depend on the association of metals with constituents of the final effluent. The removal of lead in the activated sludge pilot plant appeared to be dependent on the effective removal of suspended solids from the effluent. The metal solubilities determined in the influent and effluent samples indicate that the proportion of dissolved to total metal increased as the metal passed through the activated sludge process. This phenomenon has been noted by Oliver and Cosgrove (1974) who found that the activated sludge process was effective in removing 30 - 70% of all dissolved metals, with the exception of nickel. Chen *et al.*, (1974) found a preferential association of lead and nickel with particles in the lower part of the range of sizes found in activated sludge ($< 8\mu\text{m}$). In the case of lead these small particles may be precipitates of the metal; Barnes *et al.*, (1975) found that particle sizes of insoluble lead phosphate had a mean diameter of 0.4 - 0.6 μm . Although the removal of heavy metals by adsorption to the biomass in the activated sludge process could potentially be controlled to some degree by manipulation of the operating parameters, if some metals were to form poorly settleable particulates preferentially further optimisation of the metal removal efficiency may involve some form of effluent polishing for the removal of suspended solids such as by the use of polyelectrolytes or other types of liquid solid separators.

It is evident that one of the principal factors controlling metal removal during primary sedimentation is solubility. Soluble metals are not removed during primary sedimentation. A considerable number of complexing agents both natural and synthetic are present in raw sewage, of the synthetic complexing agents the largest single component in most sewages is contributed by the builders used in cleansing products. The presence of builders (including ion exchange materials) in sewage may significantly influence the solubility of the metals present. If a metal is sequestered by a builder the fate of the metal will depend upon the fate of the builder.

The rapid hydrolysis of STPP in the sewage matrix (Sawyer and McCarthy, 1978) results in a substantial reduction in its chelating ability. Moreover the phosphates formed as a result could potentially aid metal removal if insoluble salts are formed (Stoveland et al., 1979c).

If metals are exchanged by zeolite their concentrations in the settled sewage or in the sludge will depend on the removal efficiency of the zeolite in the primary sedimentation tanks. Suspended solids removals of 50 to 60% for a surface load of 1.25 mh^{-1} (30 md^{-1}) at dry-weather flow have been reported for U.S.A. (Water Pollution Control Federation, 1977) and this rate is comparable with that in U.K. at 3 dry-weather flow (Tebbutt, 1979). Values for suspended solids determined during 1 and 3 DWF at both concentrations of zeolite were within this range, however, during the variable flow experiments removals were considerably lower being between 20 and 30%. Influent suspended solids concentration was more important in controlling the removal efficiency than surface loading, which is consistent with previous observations (Tebbutt and Christoulas, 1975; White and Allos, 1976). This is reinforced by the poor removals observed during the experiments at variable flow when the influent sewage was diluted by rain and the influents solids were in the range 150-200 mg l^{-1} . A very strong correlation was obtained between influent suspended solids concentration and removal in all experiments, values of 0.98 and 0.99 being obtained in the six control and six test experiments respectively. This behaviour is a consequence of the flocculant settling characteristics of raw sewage (Canale and Borchardt, 1982). Since flocculation is affected by the number of particles and by the charge of the particles it is possible that the presence of zeolite could improve flocculation and enhance settling.

To permit a comparison between the removals in the control pilot plant and test pilot plant in which the influent suspended solids were always higher (by the nominal concentration of zeolite added) the relative contribution of the original (non-zeolite) suspended solids to suspended solids removal has been calculated and these values are presented in Table 46, they have been obtained by dividing the percentage removal by the initial suspended solids concentration.

Table 46 - Relative suspended solids removals in primary sedimentation at different flow conditions when zeolite was added at 30 and 60 mg ℓ^{-1}

System	Zeolite added at 30 mg ℓ^{-1}			Zeolite added at 60 mg ℓ^{-1}		
	1 DWF	3 DWF	Variable flow	1 DWF	3 DWF	Variable flow
Control	0.155	0.159	0.142	0.183	0.169	0.158
Test	0.134	0.151	0.124	0.147	0.142	0.133

It is evident from Table 46 that in the experiments where zeolite was added, the initial suspended solids contributed less to the total removal than they did in the experiments without zeolite. Using static column settling tests King et al., (1980) concluded that the removal of suspended solids was 0-20% higher in the presence of zeolite. However, from the data presented here there is no evidence of enhanced suspended solids removal in the presence of zeolite. In static column tests when zeolite was added at 30 mg ℓ^{-1} (Carrondo et al., 1981) the percentage suspended solids removal was also found to be marginally reduced from the values obtained in raw sewage when zeolite was absent.

Experiments by Carrondo et al., (1981) also indicated that the removal of zeolite in raw sewage was better than predicted by Stoke's law. This was probably the result of the flocculant nature of raw sewage, which improved zeolite removal. Removal of zeolite was only slightly influenced by hydraulic conditions and was independent of influent zeolite concentration at those concentrations examined. These observations are consistent with those of Carrondo et al., (1981) who also suggested on the basis of data from column settling tests that zeolite was removed to a lesser extent than the other suspended solids. However, the results presented here indicate that zeolite has a higher removal than the ordinary suspended solids, this difference between the two groups of results is probably the consequence of a difference in the behaviour of the particles in the static column and the dynamic test. During the dynamic test there

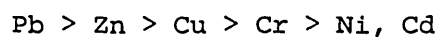
would have been more turbulence and hence more contact between zeolite and the sewage solids which would have coalesced the zeolite particles and aided their removal.

Since zeolite is substantially removed during primary sedimentation it is possible that it could improve metal removal. There are potentially two mechanisms, by aiding the flocculation and hence the removal of particles of metal or metal associated with solids or by ion exchange. From the above the former mechanism may be discounted since zeolite does not enhance the removal of the other suspended solids. The results presented here clearly indicate that when improved metal removal was observed in the presence of zeolite it was the result of ion exchange. This process is dependent on the concentrations of metals, zeolite and other ions as well as temperature and pH (Schwuger et al., 1976). Chelating agents present in the sewage (both natural and synthetic) may also compete with the zeolite for the metals. In static column tests, both Obeng et al., (1981) and King et al., (1980) concluded that zeolite would have no adverse effects on metal removal. In the experiments reported here a wide variety of sewage matrices were encountered and in some of these experiments an improvement in metal removal was observed. During the experiments when different concentrations of zeolite were added at the three flow regimes studied, influent concentrations also varied. Thus these experiments were not directly comparable, to facilitate identification of the metals whose removal was most influenced by zeolite the percentage immobilization of each metal in all experiments were calculated. This factor is the difference between the average effluent concentration in the control and test plants divided by the average influent concentration and expressed as a percentage. This eliminates effects due to variations in the influent concentration, the higher percentage immobilization the greater the effect of zeolite, these values are presented in Table 47. Those metals which on certain occasions exhibited significant differences between their concentrations in the effluent test and effluent control i.e. chromium, copper, lead and zinc may be ranked according to their percentage immobilization in Table 47.

Table 47 - Percentage metal immobilization for experiments at different flow conditions when zeolite was added at 30 and 60 mg ℓ^{-1}

Metal	Zeolite added at 30 mg ℓ^{-1}			Zeolite added at 60 mg ℓ^{-1}		
	1 DWF	3 DWF	Variable flow	1 DWF	3 DWF	Variable flow
Cadmium	-	-9.7	-18.5	3.8	-4.8	1.9
Chromium	-15	4.7	4.3	4.0	5.7	10.0
Copper	1.8	6.7	9.8	1.3	2.7	7.7
Lead	6.7	8.3	15.6	6.8	6.5	9.4
Nickel	-4.5	-13.3	0	10.0	0	-4.8
Zinc	18.8	8.2	3.4	2.2	-2.7	1.2

The following decreasing series of removal in the presence of zeolite is evident,



this does not agree completely with the series presented by Schwuger et al., (1976),



This suggests that the sewage matrix is critical in controlling the affinity of zeolite for metals and as a consequence the effect of zeolite on metal removal. This is confirmed by the lack of consistency with which these metals were influenced in the experiments reported here with the exception of lead.

NTA is a powerful chelating agent with affinities for a wide range of divalent cations including the so-called heavy metals (Snoeyink and Jenkins, 1980; Manahan and Smith, 1973). As indicated before the fate of metals chelated by NTA will depend upon the fate of NTA.

Removal of NTA during primary sedimentation has been the subject of very limited study. Removals between 11 and 58% have been reported (Thayer and Kensler, 1973). This removal is not readily explained by biological mechanisms (International Joint Commission, 1978), oxidation

seems to be unlikely because of the anoxic conditions which ordinarily prevail in primary sedimentation tanks and because of the lack of opportunity for developing an acclimatization culture, (except possibly as a result of co-settlement). In the work reported here a comparable range of removal efficiencies to those reported by Thayer and Kensler (1973) have been observed. Although removals varied between 16 and 40% most values were between 20 and 30%. It appears that the percentage removal of NTA was greatest at the highest influent NTA concentration, 30 mg l^{-1} . This observation was most probably related to variations in the sewage matrix between experiments. Moreover this conclusion would not be consistent with the result of Thayer and Kensler (1973) who found high removals at relative low influent concentrations e.g. 58% and 33% removals with influent concentrations of 4.78 mg l^{-1} and 1.95 mg l^{-1} respectively.

Removal of NTA during primary sedimentation is probably by adsorption on to settleable solids since it appears to be proportional to contact time. Experiments at 1 DWF which afforded the longest retention time yielded some of the highest removals. However there is no correlation between suspended solids removal and NTA removal. Indeed one of the lowest NTA removals, 18%, was observed in conjunction with the highest suspended solids removal, 62%. It may be significant that the settled sewage during this experiment had the highest COD observed in any experiment.

The effect of the introduction of NTA into raw sewage on metal removal during primary sedimentation does not appear to have been examined. Studies of the effect of NTA on metal removal during waste-water treatment processes have concentrated on secondary biological treatment. It is expected that the presence of NTA will solubilise metals "if biodegradation of NTA in secondary treatment processes is incompleted then inferior removal of metal would be expected" (Nilsson, 1971) and the mobilization of metals in the presence of NTA has been observed (Stoveland *et al.*, 1979a; 1979b). The ability of NTA to chelate metals in wastewaters is not in doubt therefore it is not surprising to find that it caused inferior removal of metals in the study reported here. A considerable reduction in the removals of lead, nickel and zinc was observed.

The magnitude of the effect of NTA on metal removal might well be greater at a sewage treatment works serving more industrialized catchments. Although close to London and in an urban area the concentration of metals in the influent sewage to the Hogsmill Valley Works are low by comparison to normal mixed industrial domestic sewage. The flow of industrial effluent to the Works is very low 2.6% of the Dry Weather Flow of which 30% has received pretreatment (Institute of Water Pollution Control, 1972). The influent concentrations of metals in Table 27 are more typical of a non-industrialized urban sewage when compared to those at other sewage treatment works presented in Table 6. Metals from industrial sources are generally soluble although they may become insoluble in the sewage matrix (Oliver and Cosgrove, 1974). Barth *et al.*, (1965) observed this effect on zinc where 90% of the added soluble zinc was converted to an insoluble form. During the jar tests reported here using raw sewage spiked with metals it was observed that cadmium, chromium, copper and zinc were gradually changed to an insoluble form during incubation. However, the presence of a chelating agent (NTA) resulted in the solubilization of cadmium, chromium, copper, lead and zinc when soluble metals were added to raw sewage. The addition of soluble metals to a mixed primary sludge caused an increase in the percentage solubility indicating that the insoluble ligands present were already saturated with the metals. When NTA was added metals were solubilized to a lesser extent in the sludge than in the sewage. This suggests that a competitive interaction between metal ions and inorganic and organic complexing agents exists, and such competitive interaction, similar to that studied in natural waters (O'Shea and Mancy, 1978) would certainly affect the distribution of the metal in the sewage treatment processes.

The ability of biological processes to adapt to a certain substance as a source of energy is known as acclimatization. "In many cases organisms may become acclimatized to the presence of potentially toxic materials provided the concentration is built up slowly over a period of time" (Tebbutt, 1966). It is well known that after the introduction of NTA into a previously NTA-free waste water treatment system, a period of acclimatization is frequently

necessary before NTA removal occurs at significant rates (Bouveng et al., 1968; Wei et al., 1979; Stoveland et al., 1979b). Often a lag occurs before a population of degrading organisms is established and during this time adsorption would appear to be the mechanism responsible for NTA removal. In the experiments reported here a removal(adsorption) of 25% 9 h after the commencement of NTA dosing to the activated sludge pilot plant previously free of NTA was observed. The adsorption in different mixed liquors not acclimatized to NTA indicates that there was a correlation between mixed liquor suspended solids concentration and the percentage of NTA adsorbed. According to Bouveng et al., (1968), the adsorption decreased as the biodegradation increased and thus it would appear that the major mechanism of NTA removal after the system is acclimatized to NTA is biodegradation (Swisher et al., 1967). Acclimatization periods of 16 to 31 d in lab-scale activated sludge simulations fed with synthetic sewage have been reported (Stoveland et al., 1979a) and 45 days in a field study (Shumate et al., 1970). This period is required either for enzyme induction in an organism already present in the system or the development of a population of organisms from organisms only intermittently present in the sewage (Shumate et al., 1970). During the experiments reported here it was observed that acclimatization to NTA was more rapid at higher sludge ages when the wastage rate was lower, thus it is probably that the development of a population of NTA degrading bacteria arises from an organism naturally occurring in the sewage and the development of this population is encouraged by the lower wastage rate. It would be expected therefore that acclimatization at high NTA influent concentrations requires more time for the development of the larger population of organisms able to degrade NTA, which is consistent with the results presented here. Moreover when a high NTA concentration was dosed in the pilot plant operating at 4 d sludge age no acclimatization occurred in 18 d. During this experiment the wastage rate exceeded the growth rate of the NTA degrading bacteria, thus no population could be developed and NTA removal was mainly by adsorption. As the sludge age was increased to 6 d the wastage rate was reduced to a value below the "wash out" rate and a population of organisms developed and complete biodegradation was achieved. Microorganisms acclimatized to degraded NTA can gradually adapt to degrade

higher concentrations of NTA (Shumate et al., 1970) if however the organisms were starved of NTA for a certain time then an acclimatization period would be required (Pfeil and Lee, 1968). Reduction in temperature can affect the biodegradation and the system would require a new acclimatization period. Eden et al., (1972) studying the effect of temperature on NTA biodegradation found that after a failure in biodegradation due to a decrease in temperature it took 10 d for the system to start degrading NTA after the temperature was increased.

After acclimatization a substantial amount of the influent NTA was removed during all the experiments reported here, however it appears that when the NTA loading varies biodegradation does not proceed to such high values and on some occasions substantial concentrations of NTA remained undegraded. Similar observations have been reported by Stoveland et al., (1979b) working in lab-scale activated sludge simulations, who examined the effect of both condensed phosphate and NTA shock loads and concluded that while condensed phosphate in the effluent was not increased due to a shock load the NTA concentration in the effluent was substantially increased during the shock load. It would appear that condensed phosphate was hydrolysed during the activated sludge process and this observation is in agreement with work reported by Finstein and Hunter (1967) who found a very substantial hydrolysis of condensed phosphates in the activated sludge process. The effect of shock load was more marked at low sludge age when an increase in NTA influent concentration from 7.5 to 15 mg ℓ^{-1} resulted in a peak of 2.0 mg ℓ^{-1} of NTA in the effluent. These results are in agreement with those previously reported (Renn, 1974; Shannon, 1973 and Stoveland et al., 1979b). Stoveland et al., (1979b) with a lab-scale activated sludge plant operating at 6 - 8 d sludge age observed an increase to a maximum of 4.4 mg ℓ^{-1} of NTA in the effluent when the influent was increased from 10 to 20 mg ℓ^{-1} . In the work reported here the effect of shock loading was also influenced by heavy metals in high concentrations in the influent, resulting in high NTA concentrations in the effluent.

It appears from the study presented that an increase in NTA concentration in the mixed liquor containing high metal concentrations, that NTA could release metals which inhibit its biodegradation. Inhibitory

effects of copper and cadmium and to a lesser extent nickel and chromium have been reported by Walker (1975), however other metal ions could also have this inhibitory effect (Nieboer and Richardson, 1980).

From this study it is evident that NTA can be degraded by organisms in activated sludge following a period of acclimatization which varies with the different situations, however if these organisms for some reason disappeared a new acclimatization period would again be required for them to become adapted.

It is proposed that the most readily degradable metal chelates formed by NTA will disappear first resulting in a redistribution of chelated ions to accommodate ions released during biodegradation (Warren 1974). It is for this reason that the addition of Ca or the presence of high level of water hardness can facilitate degradation of the more persistent chelates of NTA, for example those with copper (Björndal et al., 1972). This readjustment of equilibrium between ligand and metal possibly explains the slower rates of degradation for copper, cadmium, nickel and zinc reported by Warren (1974). It may also explain the longer period required for acclimatization in experiments at high metal influent concentrations reported here.

The ability of NTA to chelate metals is well established. Substantial mobilization of cadmium and copper from river sediments in the presence of NTA was observed by Banat et al., (1974). Zinc and nickel were also mobilized, but to a lesser degree. Mobilization of heavy metals from sediments by low concentrations of NTA has also been reported by Zitko and Carson (1972). The release of heavy metals from sediments was shown by Chau and Shiomi (1972) to be proportional to the NTA concentration. An increase in the solubility of cadmium, copper and nickel in settled sewage when NTA was added was reported by Björndal et al., (1972). Such increases in metal solubility reduce their affinity for sludge solids and thus their removal efficiency in biological sewage treatment plants. A deterioration in the uptake of copper and nickel by activated sludge in the presence of NTA was observed by Cheng et al., (1975). The concentration of heavy metals in the mixed liquor of activated sludge units supplied with settled sewage and NTA was found by Harkness (1973) to be lower than when no NTA was added. Renn (1974), found that when NTA was

introduced into a sewage treatment works, unacclimatized to NTA the removal efficiency of zinc was reduced from 75% to approximately zero.

The results presented here show that during the acclimatization when high concentrations of NTA were measured in the effluent from the pilot plant reduced removal of cadmium, copper, lead, nickel and zinc was observed in the test plant. Chromium removal was not affected by the presence of NTA which is consistent with the results presented by Banat *et al.*, (1974) in river sediments and by Stoveland *et al.*, (1979b) in activated sludge.

During shock loading experiments Stoveland *et al.*, (1979b) reported mobilization of cadmium, chromium, copper, lead, nickel and zinc when the NTA concentration in the effluent reached a maximum of $4.4 \text{ mg } \ell^{-1}$ due to an increase in the influent from 10 to $20 \text{ mg } \ell^{-1}$. In the experiment reported here when indigenous metals were present at 4 d sludge age an increase in NTA in the influent from 7.5 to $15 \text{ mg } \ell^{-1}$ caused a deterioration in the removal of lead, nickel and zinc. During the shock loading experiments when soluble metals were added to simulate sewage from an industrialized area, substantial reduction in the removals of cadmium, lead, nickel and zinc were observed.

In hard water NTA would be substantially biodegraded at constant influent NTA loadings, so that heavy metals could be adsorbed by the mixed liquor suspended solids (Stoveland, 1979a). Variations in influent NTA concentration to a sewage treatment plant would inevitably occur as a result of the irregular usage of products containing it. Under these conditions a portion of metals accumulated in the mixed liquor suspended solids would be mobilized into the effluent. Failure to remove heavy metals with sludges produced during sewage treatment, with consequent metallic pollution of the receiving waters, could have a variety of effects depending on the influent heavy metal concentrations to the treatment plant, dilution of the effluent by the receiving water and the use to be made of the receiving water. In areas of high water reuse metallic pollution could be such that standards for drinking water could be infringed (Table 4) rendering the water unsuitable for abstraction as a source of potable supply. Similar recommendations for waters to be used for a range of purposes including irrigation,

fisheries and cooling (Lester, 1981) could also be infringed. If the metallic pollution were relatively severe then the flora and fauna of the receiving water could be adversely affected and its self-purification ability impaired. The metal complexes discharged are remarkably stable in the water even at very dilute concentrations (Stumm, 1967).

It is desirable to protect receiving waters from metallic pollution to avoid contamination of the hydrosphere, this is critical in areas where re-use is practised. Equally it is desirable to eliminate or reduce eutrophication where it occurs. In seeking to achieve these objectives the consequences of any change in policy must be fully evaluated. It has been accepted on the basis of insufficient evidence that detergent phosphorus alone results in eutrophication and that the problem may be solved by the introduction of a non-phosphate builder. Insufficient attention has been paid to evaluation of the alternative builders and to the true role of detergent phosphorus in eutrophication.

NTA would not appear to be a suitable general replacement for STPP; its behaviour in waste water treatment processes will result in it contaminating the receiving water and usually in conjunction with heavy metals. There also exists the possibility that in some areas NTA may encourage eutrophication by making available previously limiting ions for algal growth (Bender, 1970). Moreover its carcinogenicity, although concentration dependent (International Joint Commission, 1977; Means *et al.*, 1980) make it an undesirable compound for extensive usage in a domestic product. Only in areas where eutrophication can be eliminated by removal of detergent phosphate alone, where very substantial dilution of the effluent by the receiving water is possible and where re-use is not important would the introduction of NTA be acceptable.

Zeolite type A is environmentally acceptable. Assuming that the product used in detergent formulations is of the same particulate size as that used in this study it will be removed during waste water treatment. It will have a limited impact on metal removal and will not adversely influence treatment performance. However, its effect on sludge treatment and the sludge disposal options requires evaluation. The principal limitation of zeolite type A is its efficiency as a deter-

gent builder and it will have to be used in conjunction with a co-builder (STPP or NTA) for efficient wash performance. Thus if used in conjunction with NTA it would be subject to the reservations associated with that material. If used in association with STPP the reduction in the phosphate concentration is likely to be so small as to have little effect on eutrophication in most areas. It is possible that in soft water areas where the role of the builder is less important formulations contain zeolite alone could be effective washing products, however their distribution would have to be limited to these soft water areas which could prove difficult. Zeolite may encounter "consumer resistance" because of unsightly deposits which form on clothes or because of the premature deterioration of the zinc components of washing machines by abrasion and ion exchange. If the particle size is reduced to avoid these problems or to increase the rate of calcium exchange (since it is a function of particle size) these smaller particles would not be readily removed since the sizes currently in use are a minimum for settling.

Substitution of detergent phosphorus may have a limited role to play in the control of eutrophication. However the only generally effective substitute, NTA, has more deleterious environmental effects than STPP. Phosphorus removal during sewage treatment is the most obvious solution to the control of eutrophication where the limit concentration of phosphorus in a eutrophying receiving water is being overcome by the contribution from sewage effluent alone. It should be remembered that detergents contribute approximately 30% of the phosphorus in sewage effluent and their removal alone may not result in a sufficient reduction in the phosphorus concentration to prevent eutrophication. It has been argued that even if chemical phosphorus removal from sewage effluent is necessary to prevent eutrophication the cost of treatment will be less in the areas where the detergent contribution has been eliminated. This is not necessarily true, if lime is being used for removal the quantity required is controlled more by the alkalinity of the water than the concentration of phosphate (Bouveng, 1978) thus the removal of the detergent component will have little effect on the quantity of lime required, moreover the same plant will be required thus neither capital or operating

costs will be reduced. Furthermore the introduction of chemical treatment will have a polishing effect which will enhance metal removal. It would appear therefore that where eutrophication may be limited by phosphorus, removal of phosphorus would be a more advantageous method of control than the introduction of a non-phosphate builder.

6 CONCLUSIONS

1. Heavy metal removal efficiencies in the primary sedimentation pilot plant appeared to be unaffected by variations in the influent concentrations. Removals also appeared to be unrelated to suspended solids removals, despite the probability that only particulate forms of heavy metals are removed in primary sedimentation.
2. Heavy metal removals in primary sedimentation were found to be influenced by the overflow rate. Optimum removals were found at a constant overflow rate equivalent to normal dry weather flow. A three-fold increase in the overflow rate had an adverse effect on heavy metal removal, while the poorest removals were observed when a diurnal variation in the flow was introduced. Thus, the use of balancing tanks to equalise the flow may be expected to maintain efficient heavy metal removal.
3. The removal of heavy metals in the activated sludge pilot plant appeared to be slightly lower when heavy metals were not added to the system than when solutions of metal salts were continuously added to the settled sewage. The removal efficiencies were also less variable when soluble heavy metals were added to the system and the biomass was able to immobilize relatively higher concentrations of soluble heavy metals, indicating that the metal speciation may influence removal.
4. When heavy metals were added to the settled sewage, probably resulting in more consistent distributions of metal species, removals were found to be influenced by the sludge age, with optimum removals occurring at the 12 d sludge age. This trend was reflected by the trend in the accumulation of heavy metals by the mixed liquor at different sludge ages, indicating that the capacity of the biomass to remove heavy metals was influenced by its growth rate, and that optimization of heavy metal removal could be achieved by the control of this parameter.
5. No effects of effluent COD on heavy metal removal were observed since this parameter remained fairly constant. However, the effluent suspended solids concentration appeared to influence removals when metals were not added to the settled sewage. Optimum removals of chromium, nickel, lead and zinc occurred at the lowest effluent

suspended solids concentration, while an inverse relationship between lead and zinc removals and the effluent suspended solids was observed, in addition lead, zinc and chromium were in predominantly particulate forms in the effluents, indicating that improved removals may be achieved by more efficient suspended solids removals.

6. Zeolite removal during primary sedimentation is not influenced by the influent zeolite concentration. Zeolite removals are as good as or better than the removals of the average suspended solids and its removal was only slightly influenced by hydraulic loading. The presence of zeolite did not enhance the removal of the average suspended solids nor did it influence COD removal.

7. The 25% calcium exchange zeolite used in this work enhanced the removals of lead, zinc, chromium and copper, the removals of cadmium and nickel were unaffected. It appears that the mechanism of removal was by ion-exchange with the zeolite and subsequent removal of the zeolite by sedimentation. Removals were most improved at 1 DWF when contact time was the longest and suspended solids removals higher. There was no evidence of a further increase in metal removal at the higher zeolite concentration ($30 \text{ mg } \ell^{-1}$). Zeolite did not consistently influence the removals of these metals and it is probable that the chemical matrix of the sewage is important in determining the effect of zeolite on the removal of most metals.

8. Limited removal of NTA (16 - 40%) occurs during primary sedimentation. This is a consequence of its adsorption onto settleable solids. Removals did not correlate with influent NTA concentration, the hydraulic conditions or the suspended solids removal. It would appear therefore that the chemical matrix of the sewage and in particular the nature of the suspended solids is critical in determining the removal of NTA during primary sedimentation. As a consequence of this behaviour the primary sludge will contain concentrations of NTA equally to or slightly greater than the concentrations in the raw sewage. Although some of this NTA will not be readily "available". The presence of NTA had no effect on suspended solids or COD removal.

9. The presence of NTA in the raw sewage during primary sedimentation resulted in the reduced removal of some metals, namely lead, nickel and zinc. These effects were independent of influent NTA concentration and hydraulic conditions. It would appear that the chemical nature of the sewage matrix is critical in determining the degree to which individual metals are affected by the presence of NTA. It is probable that the effect of NTA on metal removals will not be limited to lead, nickel and zinc, since in jar tests in raw sewage it enhanced the solubility of cadmium, chromium and copper and it would appear that not only the degree of any reduction in removal but also the metals affected are determined by their chemical form which is controlled by the chemical nature of the sewage matrix.

10. Bacteria capable of degrading NTA are present in the environment, the development of a sufficiently large population to substantially biodegrade the influent NTA requires a period of acclimatization. This period of acclimatization increased by high influent NTA concentrations, high influent metal concentration and low sludge ages. At 4d sludge age no acclimatization occurred but acclimatization did occur at 6 d, indicating that there will be a minimum sludge age at which an NTA degrading population can be achieved.

11. During the acclimatization period when the effluent NTA concentrations were high the removals of several metals were substantially reduced. Copper, lead, nickel and zinc were all affected in this manner, the removal of cadmium appeared to be unaffected whilst the removal of chromium was consistently improved. It is probable that the mobilization of the other metals from the mixed liquor made additional binding sites for chromium. It is evident that if NTA is first added to an activated sludge plant or if an acclimatization period is required after a temperature shock or a failure to degrade NTA due to toxic substances, then during this period removal of several metals will be significantly reduced.

12. When NTA is added as a shock load to simulate the variation in influent concentrations associated with a "wash day" the plant was unable to biodegrade all of the additional influent NTA. This effect was most marked at low sludge ages, high metals influent concentrations and independent of influent NTA concentration.

13. During the shock loading of NTA when the effluent concentrations of NTA were elevated there was a significant reduction in the removal of lead, nickel and zinc. In the cases of nickel and zinc this included mobilization of metal previously adsorbed from the mixed liquor. In sewages containing higher concentrations of cadmium than those at the Hogsmill Valley Works it would be anticipated that cadmium removal would also be adversely affected at low sludge age. Both chromium and cadmium (at high sludge age), exhibited an improvement in the removal (under these conditions, it is possible that the removal of other metals from the mixed liquor by NTA created binding sites for these two metals).

14. It appears that the effluent concentrations of NTA observed during these shock loading experiments may not be accounted for by either short circuiting of the NTA or by the formation of non-biodegradable complexes with heavy metals. Inhibition of the NTA biodegrading bacterial population must have occurred. This effect was bacteriostatic rather than bactericidal since the system was able to recover rapidly suggesting that the original bacterial population had not been drastically reduced.

15. Detergent phosphate substitution may have a limited role to play in the control of eutrophication, but eutrophication may be more effectively controlled by phosphate removal at the sewage treatment works. This will not only reduce more substantially the effluent phosphate concentrations than detergent phosphate substitution, it will also avoid the introduction of NTA, a compound whose use is less than desirable. In addition chemical removal of phosphorus will have a polishing effect on the effluent quality.

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Appendix I

Programme for primary sedimentation experiments

- 1 - Programme for zeolite type A and NTA experiments under 1 DWF and 3 DWF (Experiments I, II, IV, V, VII, VIII, X & XI).

Programme for zeolite type A and NTA experiments under constant flow condition was as follows:

DAY 1 - Plant Stabilization

- Filled the tanks with raw sewage at the flow rate chosen (1 DWF or 3 DWF), started the dosing of builders (zeolite 30 or 60 mg ℓ^{-1} or NTA 15 or 30 mg ℓ^{-1} as described in Section 3.1.6 and 3.1.7) to the test tank.
- Checked the total flow rate, and the individual flow rate of each tank, and make necessary adjustment to the position of the flow adjustment weirs, so as to obtain similar flow rate in each tank
- Reset the thermometer, checked the aspirator level, and left the plant running until Day 2
- Collected the Samples at 3 h interval automatically.

DAY 2 -

- Checked the thermometer readings, reset the thermometer
- Checked the aspirator level
- Checked the flow rate regularly
- Cleaned the weirs and troughs.

DAY 3 -

- Checked the flow rate and aspirator level regularly
- Stopped the whole system at 12:00 h and checked the temperature (maximum and minimum)
- Discharged the sludge and collected sludge samples; recorded the sludge volume
- Checked the aspirator level and estimated the amount of builder used
- Cleaned the system with tap water and put it ready for the next experiment

Appendix 1 cont.

2 - Programme for zeolite type A experiments under variable flow condition (Experiments III and VI).

For zeolite experiments under variable flow conditions the programme was slightly changed. These experiments were designed to study the hydraulic effect during variable flow condition, and the zeolite concentration was kept around 30 or 60 mg ℓ^{-1} while the flow rate was changed by using the cam. To facilitate plant operation, the period between 21:00 h to 7:00 h was set at constant flow. The programme was as follows:

DAY 1 - Plant Stabilization

- Filled the tanks with raw sewage at variable flow conditions using the pattern set by the cam (started at around 15:00 h)
Started the dosing of zeolite at the test tank (as described in Section 3.1.6)
- Checked the total flow rate, and the individual flow rate of each tank every hour, and made necessary adjustment to the position of the flow adjustment weirs, so as to obtain similar flow rate to both tanks.
- Reset the thermometer, checked the aspirator level, and left the plant running till 21:00 h
- Collected samples at 3 h intervals automatically
- At 21:00 h, set the total flow rate to around $0.15 \ell s^{-1}$, and stopped the cam movement; continued to dose zeolite.

DAY 2 -

- At 7:00 h restarted the cam movement and the variable flow pattern, kept zeolite concentration constant by varying the dosing rate continuously every hour.
- Cleaned the trough
- Checked the temperature, reset the thermometer
- Checked the flow rate continuously every hour, and cleaned the weirs if necessary
- At 3:00 h, stopped the cam movement, set the total flow rate to around $0.19 - 0.20 \ell s^{-1}$.
- At 21:00 h, changed the flow rate to around $0.15 \ell s^{-1}$.

DAY 3 -

At 7:00 h restarted the cam movement and the variable flow pattern, kept zeolite concentration constant by varying the dosing rate continuously, and proceeded at DAY 3, Programme 1.

3 - Programme for NTA experiments under variable flow condition (Experiments IX and XII).

These experiments were designed to simulate the diurnal variation of condensed phosphate concentration in raw sewage under variable flow condition. NTA was dosed at variable rate to achieve a peak concentration at 23:00 h or 24:00 h while the flow in the plant was changed by using the cam. The programme was as follows:

DAY 1 - Plant Stabilization

- Filled the tanks with raw sewage at 1 DWF condition (started at around 15:00 h), started dosing of NTA to the test tank
- Checked the total flow rate, and individual flow rate for each tank, and made any necessary adjustment to the position of flow adjustment weirs, so as to obtain similar flow rate to both tanks
- reset the thermometer, checked the aspirator level, and left the plant running till 21:00 h.
- Collected the samples at 3 h intervals automatically
- At 21:30 h, set the total flow rate to around 0.15 l s^{-1} , with NTA at 15 mg l^{-1} or 30 mg l^{-1} .

DAY 2 -

- At 7:00 h, started the cam movement and the variable flow pattern, dosing NTA at variable concentrations by varying the dosing rate continuously.
- Cleaned the trough
- Checked the thermometer readings, and reset the thermometer
- Checked the flow rate continuously every hour, and cleaned the weirs if necessary
- From 18:00 h onwards, started sample collection at a more frequent interval, at every $1\frac{1}{2}$ h, until 9:00 h on Day 3

DAY 3 -

- Proceeded as Day 3, Programme 1.

Appendix II - Sequence of experiments undertaken, in chronological order.

Exp. no.	Start Date	End Date	NTA conc. mg ℓ^{-1}	Sludge age, d	Metal	Phase
III	15.6.79	24.6.79	0	12	-	Stabilization at sludge age
	25.6.79	5.7.79	7.5	12	-	Acclimatization
	6.7.79	8.7.79	15	12	-	Washday simulation
II	9.7.79	22.7.79	7.5	9	-	Acclimatization
	23.7.79	25.7.79	7.5-15	9	-	Variable dosage
	26.7.79	29.7.79	7.5	9	-	Acclimatization
	30.7.79	1.8.79	15	9	-	Washday simulation
I	4.8.79	15.8.79	0	4	-	Stabilization at sludge age
	16.8.79	2.9.79	7.5	4	-	Acclimatization
	3.9.79	6.9.79	15	4	-	Washday simulation
IV	10.9.79	19.9.79	0	9	-	Stabilization at sludge age
	20.9.79	24.9.79	0	9	+	Acclimatization
	25.9.79	7.10.79	7.5	9	+	Acclimatization
	8.10.79	11.10.79	15	9	+	Washday simulation
VIII	5.5.80	15.5.80	0	9	-	Stabilization at sludge age
	16.5.80	3.6.80	15	9	-	Acclimatization
	4.6.80	6.6.80	30	9	-	Washday simulation
VI	7.6.80	17.6.80	15	9	+	Acclimatization
	18.6.80	26.6.80	30	9	+	Washday simulation
IX	28.6.80	30.6.80	0	4	+	Stabilization at sludge age
	1.7.80	17.7.80	15	4	+	Acclimatization
	19.7.80	30.7.80	15	6	+	Acclimatization
X	11.8.80	15.8.80	0	4	-	Stabilization at sludge age
	16.8.80	3.9.80	15	4	-	Acclimatization
	4.9.80	5.9.80	15	4	+	Metal shock loading
VII	1.10.80	8.9.80	0	12	+	Stabilization at sludge age
	9.10.80	9.11.80	15	12	+	Acclimatization
	10.11.80	13.11.80	30	12	+	Washday simulation
V	13.11.80	23.11.80	15	4	+	Acclimatization
	24.11.80	28.11.80	30	4	+	Washday simulation

+ Metal added

- No metal added

Appendix III Modification of the Standard Method (Government of Great Britain, 1972) for Chemical Oxygen Demand determination as suggested by Matthews (1977).

Apparatus:

11 unit - 100 ml round bottom flask "Pyrex" (quickfit No. QFR WO/3M)
11 unit - side arm adaptor (Quickfit No. Q- MF 18/3)
11 unit - cold finger condenser (Quickfit No. Q- MG 18/3)
1 unit - Sandbath (Cat. No. BLD - 350 - 0) (Gallenkamp, London, U.K.)
aluminium cover.

Reagents:

Oxidizing mixture: 7.5 g silver sulphate were dissolved in 750 ml analar sulphuric acid; 7.6618 g of potassium dichromate were dissolved in distilled water and the solution was made up to 1ℓ ; 200 ml of potassium dichromate solution were poured into a 1ℓ beaker which was placed in cold water; 750 ml of silver sulphate-sulphuric acid solution were then added slowly while stirring; the mixture was cooled and stored in a brown glass bottle.

Mercuric sulphate solution: 50 g mercuric sulphate were dissolved in 225 ml distilled water; 25 ml analar sulphuric acid were then added slowly while stirring.

Ferrous Ammonium Sulphate: 0.0625 N solution was prepared by dissolving 24.5 g ferrous ammonium sulphate in distilled water. The solution was made up to 1ℓ with distilled water and 20 ml analar sulphuric acid. This solution was standardised every time it was used against a potassium dichromate standard solution.

Standardisation of Ferrous Ammonium Sulphate: 20 ml of standard potassium dichromate solution (0.0125 N) and 3 ml of concentrated sulphuric acid were used to titrate against the ferrous ammonium sulphate solution. The potassium dichromate solution was prepared by dissolving 1.2259 g of potassium dichromate (predried at 105°C for 2 h) into 2ℓ distilled water.

Appendix III cont.

Procedure:

A 2 ml of raw sewage or settled sewage plus 3 ml of distilled water or 5 ml of final effluent sample were pipetted into each reaction flask; in another flask 5 ml distilled water was added to act as blank. 0.5 ml mercuric sulphate solution were added to each flask. 9.5 ml oxidizing mixture were added to each flask. The adaptor and cold finger condenser were connected to each reaction flask.

The contents were refluxed in the enclosed sand bath for 2.25 h.

The flasks were allowed to cool for 15 min, the cold finger condensers rinsed into the flasks and the remaining dichromate titrated against ferrous sulphate using two drops "Ferroin" indicator.

The COD of the sample was then given by:

$$\text{COD} = \frac{8\,000\,N(V_1 - V_2)}{V_s} \text{ mg } \ell^{-1}$$

where: N is the normality of ferrous ammonium sulphate

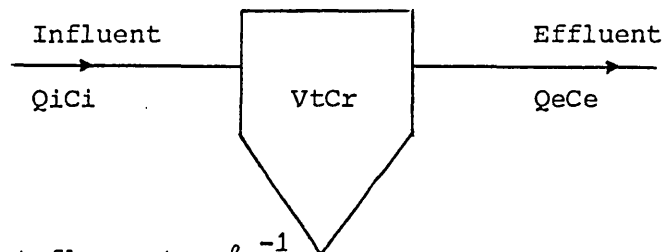
V_1 is the volume of ferrous ammonium sulphate required for the blank titration, ml.

V_2 is the volume of ferrous ammonia sulphate required for sample titration, ml.

V_s is the volume of sample, ml.

Appendix IV

Percentage removal and mass balance for primary sedimentation pilot plant



where

Q_i = Influent flow rate, l s^{-1}

C_i = mean metal concentration in the influent, $\mu\text{g l}^{-1}$

Q_e = Effluent flow rate, $\text{l s}^{-1} = Q_i$

C_e = mean metal concentration in the effluent, $\mu\text{g l}^{-1}$

V_t = volume of liquid (sludge + supernatant) in the tank, l

C_r = mean metal concentration in the liquid (sludge + supernatant), $\mu\text{g l}^{-1}$

t = total time for the experiment, s

Percentage Removal

Method 1 - Based on the influent and effluent metal concentrations since sludge was not discharged during the experiment

$$\% \text{ Removal 1} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e calculated from 3 h samples.

Method 2 - Based on the influent and liquid (sludge + supernatant) remaining in the tank metal concentrations

$$\text{Total volume treated} = Q_i \times t$$

$$\text{Metal input} = Q_i \times t \times C_i$$

$$\text{Metal retained in the tank} = V_t \times C_r$$

$$\% \text{ Removal 2} = \frac{V_t \times C_r}{Q_i \times t \times C_i} \times 100$$

where C_i obtained from influent composite sample

Method 3 - Similar to Method 1 but C_i and C_e calculated from composite samples.

Appendix IV cont.

Mass Balance

$$\text{Metal input} = Q_i \times t \times C_i$$

$$\text{Metal output} = Q_i \times t \times C_e$$

$$\text{Metal retained in the tank} = V_t \times C_r$$

$$\% \text{ Balance} = \frac{Q_i \times t \times C_i}{Q_i \times t \times C_e + V_t \times C_r} \times 100$$

Example : Chromium in control unit, experiment using 30 mg ℓ^{-1} zeolite at 1 DWF.

$$\% \text{ Removal 1} = \frac{16.8 - 11.3}{16.8} \times 100 = 33\%$$

$$\% \text{ Removal 2} = \frac{946.7 \times 267}{0.112 \times 165600 \times 40.4} \times 100 = 17\%$$

$$\% \text{ Removal 3} = \frac{40.4 - 32}{40.4} \times 100 = 21\%$$

$$\text{Mass Balance} = \frac{0.112 \times 165600 \times 40.4}{946.7 \times 267 + 0.112 \times 165600 \times 32} \times 100 = 104$$

Appendix V - Variation of filtered phosphates in raw sewage

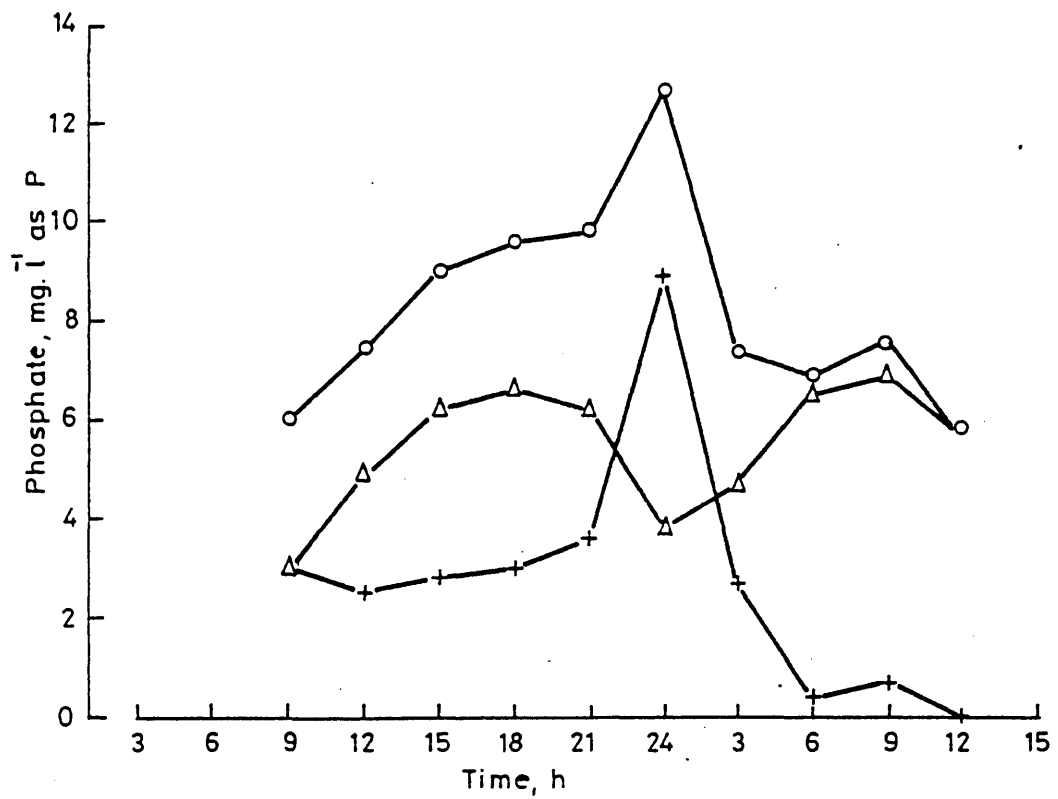


Figure 43 - Daily variation of total (-O-), ortho (-Δ-) and condensed (-+-) phosphates in raw sewage

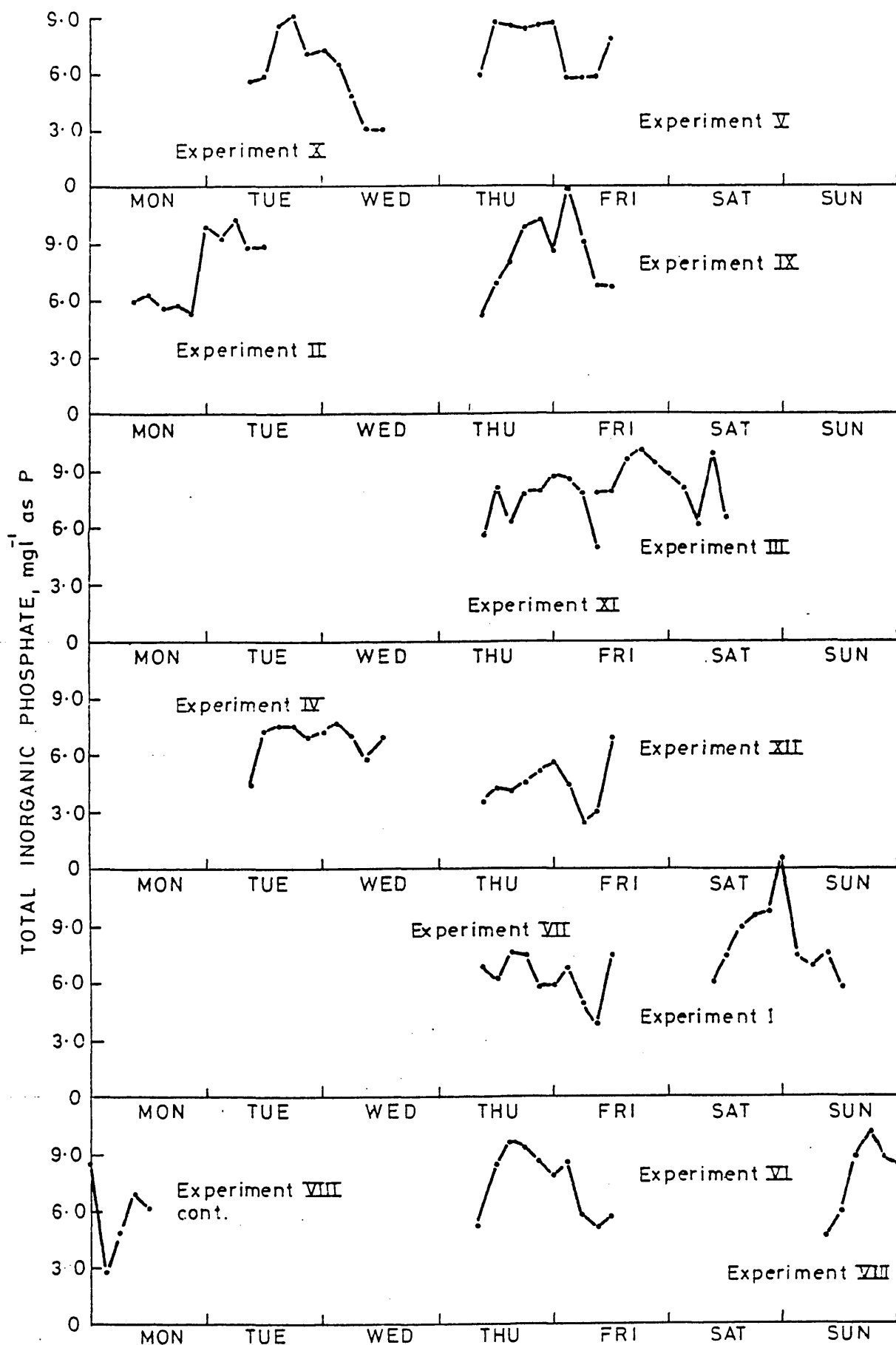


Figure 44 - Total inorganic phosphate concentrations in raw sewage during primary sedimentation simulations

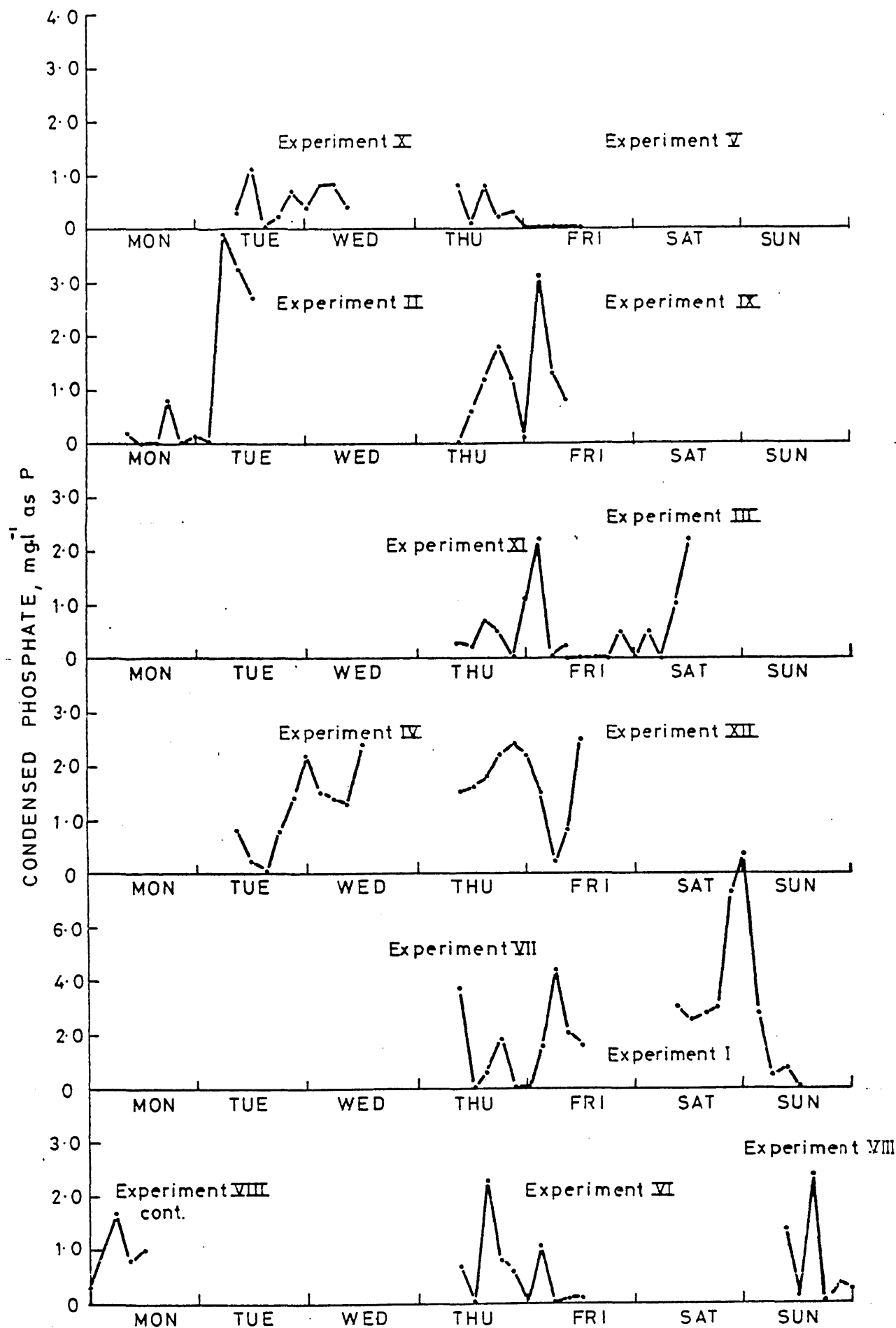


Figure 45 - Condensed phosphate concentrations in raw sewage during primary sedimentation simulations

Table 48 - Treatment parameters during experiments with low metals and low NTA influent concentrations at different sludge ages during the acclimatization period preceeding the "wash day" simulation.

Parameter	System	4 d sludge age			9 d sludge age			12 d sludge age		
		mean	RSD %	range	mean	RSD %	range	mean	RSD %	range
MLSS mg ℓ^{-1}	Aerator Control	1641	12	1345-1990	2934	14	2060-3305	3687*	9.3	3120-4220
	Aerator Test	1555	11	1270-1835	3230	9.0	2635-3555	3385*	8.5	2990-3760
MLVSS mg ℓ^{-1}	Aerator Control	1569	11	1345-1780	2596	11	2060-2680	3232*	7.2	2905-3675
	Aerator Test	1478	12	1175-1705	2901	7.6	2575-3280	2980*	5.4	2660-3235
SS mg ℓ^{-1}	Effluent Control	10	19	8- 13	4.6	81	1.0- 9.5	17	86	0.1- 46
	Effluent Test	8	76	1-16.5	3.9	105	1.0-13.5	15	80	2.5- 38
SVI $\text{m}\ell \text{ g}^{-1}$	Aerator Control	391	23	190- 463	71	17	64- 102	215	20	148- 274
	Aerator Test	366	30	261- 575	70	2.8	66- 72	219	21	153- 283
pH	Influent	7.69	0.1	7.68-7.70	7.55	2.1	7.35-7.75	7.68	0.1	7.60-7.75
	Effluent Control	7.58	3.0	7.41-7.89	7.58	1.0	7.51-7.67	7.48	0.5	7.45-7.51
	Effluent Test	7.73	2.0	7.58-7.96	7.58	1.0	7.54-7.61	7.50	0.4	7.47-7.53
NH_3 mg ℓ^{-1} as N	Influent	36	24	19- 49	26	40	13- 39	39	11	35- 43
	Effluent Control	10*	79	1.2- 24	5.1	130	0.1- 15	2.6	69	0.9- 4-4
	Effluent Test	16*	54	5.8- 29	2.9	136	0.1- 8.4	3.7	95	0.2- 7.2
COD mg ℓ^{-1}	Influent	194	14	138- 219	231	17	209- 276	240	9.7	204- 268
	Effluent Control	46*	12	38- 55	48	25	28- 66	49	12	40- 59
	Effluent Test	58*	17	42- 71	43	21	29- 52	46	10	38- 53
F/M [†]	Aerator Control	0.63	10	0.57-0.73	0.46	31	0.27-0.66	0.36*	11	0.32-0.43
	Aerator Test	0.61	13	0.52-0.73	0.38	22	0.23-0.47	0.40*	16	0.34-0.52

* Indicates that the values for control and test are different at 5% level of significance

† food to micro-organism ratio calculated based on COD

Table 49 - Treatment parameters during experiments at 9 d sludge age and different metals and NTA influent concentrations during the acclimatization period preceeding the wash day^a simulation.

Parameter	System	9 d sludge age, Low NTA, High Metal			9 d sludge age, High NTA, Low Metal		
		mean	RSD %	range	mean	RSD %	range
MLSS ⁻¹ mg ℓ^{-1}	Aerator Control	3159	15	2325-3740	3590	6.6	3150-4075
	Aerator Test	3102	8.6	2785-3595	3540	5.6	3160-3925
MLVSS ⁻¹ mg ℓ^{-1}	Aerator Control	2773	16	2035-3255	3210	7.2	2850-3700
	Aerator Test	2816	7.4	2495-3060	3161	6.4	2870-3565
SS mg ℓ^{-1}	Effluent Control	11	52	5- 18	17	37	7- 28
	Effluent Test	14	36	9- 21	16	36	7- 23
SVI mg ℓ^{-1}	Aerator Control	267	24	374- 202	164	27	98- 221
	Aerator Test	277	14	321- 211	165	24	106- 218
pH	Influent	7.55	0.5	7.49-7.60	7.57	2.2	7.20-7.84
	Effluent Control	7.47	0.7	7.39-7.54	7.34	1.8	7.12-7.47
	Effluent Test	7.47	1.0	7.38-7.59	7.34	1.6	7.12-7.52
NH ₃ mg ℓ^{-1} as N	Influent	36	22	23- 45	37	31	18- 55
	Effluent Control	17	22	12- 20	15	51	2.9- 29
	Effluent Test	17	22	11- 21	17	67	2.5- 40
COD mg ℓ^{-1}	Influent	202	14	171- 242	221	28	136- 338
	Effluent Control	43	29	30- 67	49	46	13- 84
	Effluent Test	39	26	20- 50	55	33	19- 77
F/M [†]	Aerator Control	0.36	11	0.32-0.40	0.32	30	0.21-0.45
	Aerator Test	0.37	11	0.33-0.41	0.32	30	0.22-0.48

† food to micro-organism ratio calculated based on COD

Table 50 - Treatment parameters during experiments with high metals and high NTA influent concentrations at different sludge ages during the acclimatization period preceeding the "wash day" simulation.

Parameter	System	4 d sludge age			9 d sludge age			12 d sludge age		
		Mean	RSD %	range	mean	RSD %	range	mean	RSD %	range
MLSS mg ℓ^{-1}	Aerator Control	2182	9	1940-2410	2640*	10	2665-2875	3742	13	2715-4465
	Aerator Test	2427	3	2330-2465	2964*	7.8	2765-3355	3822	11	2375-4210
MLVSS mg ℓ^{-1}	Aerator Control	1965	10	1755-2250	2426*	13	1885-2675	3304	14	2460-4115
	Aerator Test	2208	5	2050-2240	2715*	8.0	2460-3060	3331	13	2060-3755
SS mg ℓ^{-1}	Effluent Control	3.0	50	0.5- 4.5	13	26	9.0- 19	13	41	2.0- 22
	Effluent Test	4.8	28	2.5- 6.0	15	28	7.0- 18	10	41	5.0- 19
SVI mL g^{-1}	Aerator Control	104	10	93- 120	129	16	108- 149	126*	31	85- 189
	Aerator Test	106	5	102- 117	112	20	89- 134	162*	17	101- 219
pH	Influent	7.64	3.0	7.40-7.87	7.77	1	7.69-7.91	7.60	2.3	7.16-7.81
	Effluent Control	7.32	0.3	7.29-7.34	7.06	1	6.98-7.19	7.13*	1.4	6.98-7.29
	Effluent Test	7.32	0.9	7.25-7.39	7.25	3	7.02-7.56	7.16*	1.6	6.97-7.30
NH ₃ mg ℓ^{-1} as N	Influent	17	28	13- 22	28	30	14- 35	22	38	36- 4.2
	Effluent Control	13	94	0.9- 13	0.5	62	0.2- 1.0	1.1	183	8.4- 0.1
	Effluent Test	6.3	98	0.1- 13	1.0	87	0.1- 2.3	0.8	195	5.8- 0.1
COD mg ℓ^{-1}	Influent	285	3.2	276- 294	245	38	119- 391	270	29	146- 328
	Effluent Control	57	16	48- 66	56	14	42- 69	66	43	31- 111
	Effluent Test	53	11	47- 59	49	9.7	44- 57	63	35	34- 103
F/M [†]	Aerator Control	0.70	7.9	0.64-0.75	0.60	13	0.52-0.67	0.33	28	0.21-0.50
	Aerator Test	0.67	3.0	0.65-0.69	0.59	17	0.49-0.69	0.32	26	0.20-0.45

* Indicates that the values for control and test are different at 5% level of significance

† food to micro-organism ratio calculated based on COD

Appendix VII

Estimation of metal mobilization from the fibre glass sedimentation tanks.

An experiment was undertaken, as described in section 3.9 to determine if there was any metal mobilization from the fibre glass used in the construction of the sedimentation tanks, in the presence of NTA. Samples were collected 1 min before the addition of NTA and 1, 2 and 3 h after the addition had been made, they were analysed 4 times and the average value taken. The results were treated statistically using variance ratio test (F). Variance ratio for different metals were 1.38 for cadmium, 0.19 for chromium, 0.53 for copper, 0.22 for lead, 0.04 for nickel and 0.49 for zinc. Comparing these results with the F value of 3.49 ($n_1 = 3$, $n_2 = 12$) at 5% level of significance it may be concluded that NTA has no significant effect on the mobilization of metal from the fibre glass at the concentrations used during these experiments.

Appendix VIII

Some operational parameters at Hogsmill Valley Works.

Table 51 - Mean values for some operational parameters at Hogsmill Valley Sewage Treatment Works (Thames Water Authority, U.K.) from April 1979 to February 1981.

Treatment	Parameters	Period of Observation	
		April 1979- March 1980	April 1980- February 1981
Primary Sedimentation	Effluent SS mg l^{-1}	105	106
	SS Removal %	71.4	70.5
	Effluent COD mg l^{-1}	276	282
	Effluent BOD mg l^{-1}	149	145
	COD/BOD	1.852	1.945
	Effluent NH_3 mg l^{-1} as N	29	34
	Effluent total hardness* in mg l^{-1} as CaCO_3	305	290
Activated Sludge and Secondary Sedimentation	Effluent SS mg l^{-1}	12.3	11.8
	SS Removal %	88	89
	Effluent COD mg l^{-1}	46	44
	Effluent BOD mg l^{-1}	11.2	6.4
	COD/BOD	4.107	6.875
	Effluent NH_3 mg l^{-1} as N	7.7	8.0
	Sludge age d	6.2	6.0

* determined from grab samples

Appendix IX

Effect of the addition of NTA on the Alkalinity of the settled sewage.

An experiment was carried out to determine the effect of NTA at various concentrations on the alkalinity of settled sewage (as described in section 3.4 and the results are shown in Table 52).

Table 52 - Effect of the addition of NTA on the alkalinity of settled sewage

Concentration of NTA (mg l^{-1})	Alkalinity (mg l^{-1} as CaCO_3)
0	346.0
7.5	350.5
15.0	353.5
37.5	357.5

It was expected that the addition of NTA in the form of its sodium salt would increase slightly the alkalinity, however, the increase of 3.2% due to the addition of 37.5 mg l^{-1} of NTA was very small and would not cause any significant interference in biological activity of the ML or the hydrolise of some metallic ion causing its removal.