

The effects of some common inorganic soil components on the pyrolytic analysis of plastics

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ABSTRACT

Plastics and microplastics are major hazards for the environment and human health. Plastic materials in the sedimentary record are a marker for modern anthropogenic activity. One environmental reservoir of plastics and microplastics is soil. One method to detect the presence of plastics in soil, and to thereby recognise the presence of its hazards, is pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Yet soils are multicomponent mixtures and any analytical artefacts generated will reduce our ability to monitor the presence of plastics. We have studied the Py-GC-MS responses for the polymers polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC), in the presence of individual phyllosilicate (kaolinite, illite and montmorillonite) and iron oxyhydroxide/oxide (goethite and magnetite) minerals that may be present in soil. Our data show the distinctive polymer fingerprint becomes obscured when analysed with minerals. We have isolated the effects of some potential inorganic soil components so that responses from complex matrices can be deconvolved. The mineral-assisted aromatisation of compounds affects the diagnostic signals of the original polymer, particularly for those polymers (PE and PP) which have a large aliphatic hydrocarbon signature when analysed alone. Iron oxyhydroxide/oxide are shown to have a greater effect on the data than phyllosilicates. Our results will help guide future interpretations of Py-GC-MS data obtained when monitoring soils for plastic contamination. Py-GC-MS is most commonly applied as a qualitative method, yet detailed quantitation of the organic-inorganic reactions we have described, albeit analytically complex, would represent a useful future study.

1. Introduction

The generation of plastic debris is a relatively recent phenomenon and can be used as a stratigraphic marker in the sedimentary record. The period from 1945 onwards can be identified by an increase in plastic materials [1] and represents a marker for the Anthropocene [2]. Over 300 million tonnes of plastic are produced each year and a significant proportion of this amount is transferred to the environment [3,4].

During transport and storage, plastic debris is subject to the effects of physical, chemical, biological, and photolytic degradation mechanisms which lead to fragmentation into smaller particles [5]. Eventually plastic debris is reduced to a size that is undetectable to the naked eye and microplastics are formed. Plastics and microplastics in the environment have implications for human health [6]. Plastics may contain toxic chemicals, used during their production, that can be transported to and through the environment [7,8]. Plastic can also act as a sorbent for toxic materials such as polychlorinated biphenyls [9] and heavy metals [10,11]. Plastics and their associated chemicals can also be taken up by

algae [12] and enter the food chain [11,13].

It is becoming increasingly apparent that the degradation products of plastic debris are recognised as a problem for our soils [14–16]. Sources of plastic for soil environments include plastic mulching [17], sewage-derived soil amendments [18], composts [19], and atmospheric input [3,20]. Once in the soil, the products of plastic degradation persist for decades [3].

Effective tracking is required both to monitor and mitigate these plastic pollution processes. Effective methods for the analysis of plastics and microplastics in soil include infrared or Raman spectroscopy and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) [21–23]. Py-GC-MS has been used to analyse the plastic content of environmental samples such as sediments in coastal areas [24,25]. Compound ratios in soil pyrolysates can reveal the presence of plastics [26]. Indicators of polystyrene and polystyrene containing polymers (e.g. SBR) in soil are the appearance of styrene dimers and trimers in the pyrolysates [27]. The styrene dimer and trimer degradation products, as well as the toluene/styrene ratio, have been used to detect and quantify polystyrene in

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natural organic matter, such as soil [28]. The use of Py-GC-MS to analyse plastics and microplastics in soils needs to be optimised with a full understanding of any artefacts that are generated owing to the chemical constitution of the soil matrix.

The influence of mineral matrices on the chemical constitution of pyrolysates has been explored for organic matter in sedimentary rocks [29–31], and similar approaches are used in this study to enable the monitoring of plastic contamination in soils. Previous studies have examined the effects of minerals on the pyrolysis of polymers, however they have been limited to the study of single polymers [22,32], rather than a comprehensive study of the effects of a range of minerals on a variety of polymers. The inorganic sample matrix has been shown to greatly affect the pyrolysis response for polyethylene terephthalate (PET) [33]. In this study, we analyse four of the most widely used polymers, polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC), as pure samples, and in mixtures containing minerals. The minerals used in this study were chosen as they are common components found in soils; kaolinite, illite and montmorillonite are common constituents of clays, while goethite is the most ubiquitous iron oxide found in soils [34]. The isolated effects of some of these potential inorganic soil components on plastics analysed by Py-GC-MS will aid in the interpretation and deconvolution of responses from complex matrices such as soils.

2. Materials and methods

2.1. Samples

Polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC) were obtained in powder form from Sigma Aldrich. Na-rich montmorillonite (SWy-2), illite (IMT-1) and kaolinite (KGa-1b) were obtained from the Source Clay Repository of the Clay Minerals Society. Magnetite and goethite were obtained from Sigma-Aldrich.

Samples were ground to a powder using a pestle and mortar. Mixtures of polymer and clays were composed of 2 % w/w polymer and 98 % w/w clay or iron oxide.

2.2. Pyrolysis-gas chromatography-mass spectrometry

For pyrolysis experiments, samples (0.4 mg) were placed in quartz pyrolysis tubes plugged with quartz wool at each end. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was performed using a 2000 Pyroprobe (CDS Analytical) fitted via a CDS 1500 valve interface. Samples were heated to 650 °C, at a rate of 20 °C ms⁻¹, and held there for 15 s, in a flow of helium. The pyrolysis unit was coupled to a 6890 gas chromatograph coupled to a 5973 mass spectrometer (both Agilent Technologies). The GC inlet was held at 270 °C. Separation was performed on a DB-5 ms ultra inert column (J&W; approximately 30 m x 0.25 mm x 0.25 µm), operated in split mode (10:1) with a helium column flow rate of 1.1 ml min⁻¹. The gas chromatograph oven was held at an initial temperature of 40 °C for 2 mins, then increased at a rate of 5 °C min⁻¹ to reach a final temperature of 310 °C, which was held for 10 mins.

Mass spectra were acquired over the range *m/z* 45–550. Identification of peaks in the chromatograms was carried out using the Agilent MSD Chemstation software with comparison to the NIST mass spectral library, characterised samples, standards, custom libraries and comparison with the literature [35]. Repeat experiments (at least two for each sample) revealed relatively consistent results with relative responses for key compounds (e.g. 2,4,6-trimethyl-1-nonene and 2,4,6,8-tetramethyl-1-undecene in PP) varying by less than 1 % between analyses.

3. Results

3.1. Py-GC-MS of polyethylene

Fig. 1a shows the Py-GC-MS products of PE alone, which produced a repeating series of triplet peaks, consisting of *n*-alkadienes, *n*-alkenes and *n*-alkanes. The *n*-alkene peak was the largest of the three, with the *n*-alkadiene and *n*-alkene peaks being of a similar size. *n*-alkenes were detected in the series C₆ to C₃₃, whereas alkanes and alkadienes were detected from C₈ to C₃₃.

A range of different mineral-induced effects were observed when PE (2 % w/w) was pyrolyzed in the presence of phyllosilicate minerals and iron oxides. It should be noted that the minerals were also analysed on their own, and they provide no contribution to the pyrolytic profiles of the polymers. Fig. 1b shows the pyrolysis products of PE mixed with the phyllosilicate kaolinite. Compared to PE analysed alone, the alkadiene peaks were no longer detected when PE was mixed with kaolinite, however the alkene/alkane doublet was still detected and this was reduced to the alkane component at higher retention times,

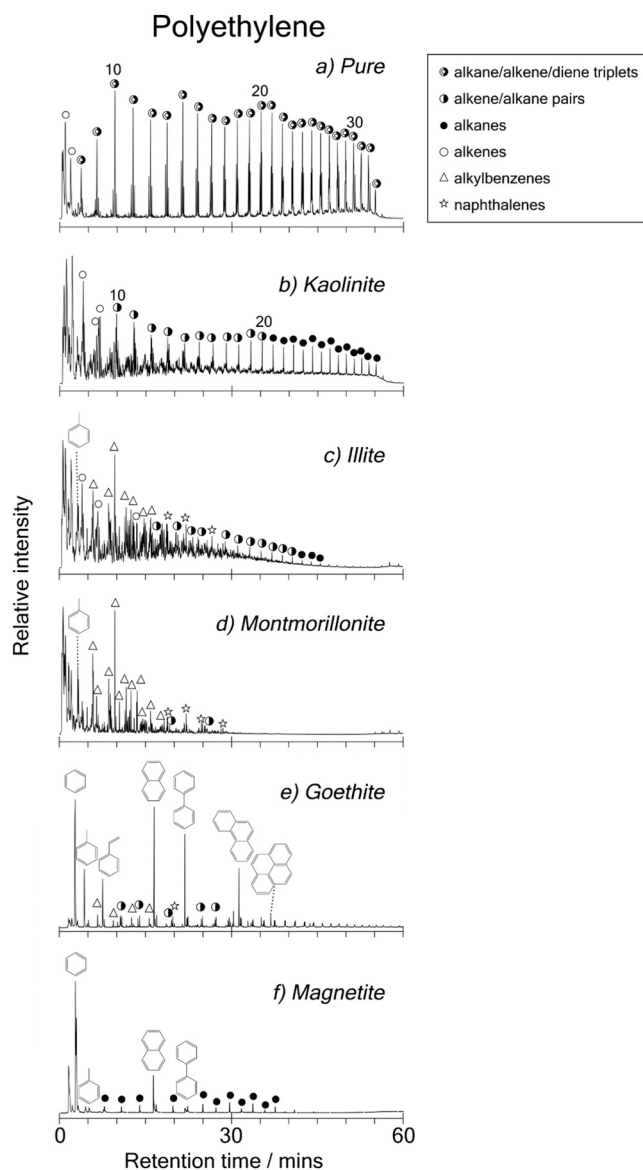


Fig. 1. Py-GC-MS total ion chromatograms of (a) polyethylene, and polyethylene (2 % w/w) mixed with (b) kaolinite, (c) illite, (d) montmorillonite, (e) goethite and (f) magnetite, all pyrolyzed at 650 °C.

approximately equivalent to the elution of the C₂₁ homologues of these compounds. In the presence of kaolinite, the alkene/alkane distribution was also skewed towards the shorter chain lengths and branched chain hydrocarbons were observed at the lower retention times. PE mixed with illite, Fig. 1c, displays even more differences to PE analysed alone. A large number of aromatic molecules were observed, namely toluene and alkylbenzenes, as well as methylnaphthalenes. Alkene/alkane doublets were still observed but their intensity was much reduced.

The final phyllosilicate analysed in this study, montmorillonite, generated pyrolysis products that were almost unrecognisable from those produced by pure PE. Fig. 1d shows that the TIC was dominated by alkylbenzenes, in particular trimethyl-benzene, and alkylnaphthalenes were also detected. A very small amount of aliphatic hydrocarbon signal remained.

In contrast to PE mixed with phyllosilicates, PE mixed with iron oxides displayed quite different results, and the pyrolysis products were dominated by aromatic molecules. For PE mixed with goethite (Fe(III) oxyhydroxide) (Fig. 1e) some of the original hydrocarbon alkene/alkane background signal remained but was greatly reduced in intensity compared to the pure PE sample. Instead, large peaks were observed for benzene, toluene, styrene, naphthalene, biphenyl and phenanthrene. Smaller peaks were observed for alkylbenzenes and methyl-naphthalene. Fig. 1f shows pyrolysis products from PE mixed with magnetite (Fe(II,III) oxide) revealing that some alkane backbone was evident but that the products were dominated by benzene and naphthalene.

3.2. Py-GC-MS of polypropylene

Fig. 2 shows the Py-GC-MS of PP analysed alone and mixed with phyllosilicates and iron oxides. PP analysed alone, Fig. 2a, shows a series of peaks corresponding to branched-chain alkenes, from 2-methyl-1-pentene (C₆H₁₂), all the way up to approximately C₃₈H₇₈. The most intense peaks were observed for the trimer (2,4-dimethyl-1-heptene) and pentamer (2,4,6,8-tetramethyl-1-undecene). Only one peak was observed for 2,4-dimethyl-1-heptene, however three peaks were observed for 2,4,6,8-tetramethyl-1-undecene owing to its different diastereoisomer forms (isotactic, heterotactic and syndiotactic) [35,36].

PP mixed with phyllosilicates produced quite different results for each phyllosilicate investigated, with an increasing amount of aromatic compounds detected in the order kaolinite < illite < montmorillonite, similar to the increasing aromaticity observed for PE mixed with phyllosilicates. PP mixed with kaolinite, Fig. 2b, displayed a broad, decreasing, distribution of branched alkenes, and at higher retention times, alkanes. These data were in contrast to pure PP which showed discrete repeating units of the polymer. The addition of kaolinite to PP caused rearrangements of the polymer units. A few alkylbenzenes were also detected.

Fig. 2c shows PP mixed with illite. Similar to PP mixed with kaolinite, when PP is mixed with illite a broad distribution with a range of branched aliphatic hydrocarbons were detected, however there were some clearly defined peaks from aromatic compounds such as alkylbenzenes and alkylnaphthalenes. The dominant peaks corresponded to trimethyl-, tetramethyl- and pentamethyl-benzenes. In the third phyllosilicate investigated, montmorillonite, shown in Fig. 2d, no aliphatic hydrocarbons were detected, instead the TIC was dominated by aromatic molecules, namely alkylbenzenes and alkylnaphthalenes. Again, trimethyl-, tetramethyl- and pentamethyl-benzenes were the dominant peaks.

The TIC of PP mixed with the iron oxide goethite, shown in Fig. 2e, was unrecognisable from the TIC obtained from PP analysed alone; the data displayed dominant peaks from alkylbenzenes, in particular dimethyl- and trimethyl-benzene. Alkenes, alkanes and methylnaphthalene were also detected from the PP and goethite mixture. Fig. 2f shows PP mixed with the iron oxide magnetite, which generated different results to that of PP mixed with goethite. A large number of

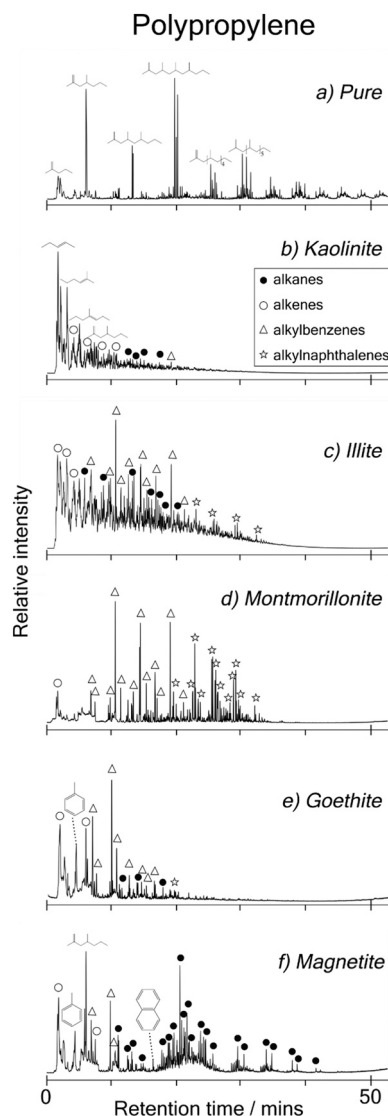


Fig. 2. Py-GC-MS total ion chromatograms of (a) polypropylene, and polypropylene (2 % w/w) mixed with (b) kaolinite, (c) illite, (d) montmorillonite, (e) goethite and (f) magnetite, all pyrolyzed at 650 °C.

aliphatic hydrocarbons were detected, however in contrast to pure PP where alkenes were detected, when PP is mixed with magnetite straight and branched-chain alkanes were observed. The aromatic molecules toluene, trimethyl-benzene and naphthalene were also detected.

3.3. Py GC-MS of polystyrene

The pyrolysis products from PS alone, Fig. 3a, were dominated by styrene, α -methylstyrene, styrene dimer ((2,4-diphenyl-1-butene), styrene trimer (2,4,6-triphenyl-1-hexene) and styrene tetramer [27,37]. Other aromatic molecules such as benzene, indene, bibenzyl (1,2-diphenylethane) and 1,2-diphenylpropane were also detected.

When PS was mixed with the phyllosilicates, kaolinite, illite and montmorillonite, styrene and α -methylstyrene were still detected with relatively high intensities, however, changes were observed to the TICs, particularly in the higher retention time period. A large peak was observed for diphenylcyclopropane for all three phyllosilicates. Ethylbenzene, methylindene, diphenylmethane, diphenylethane, phenylnaphthalene, benzo fluorene and other multi-ring aromatic molecules were also detected. All TICs of PS mixed with the phyllosilicates show similar results, however there were a few differences observed between

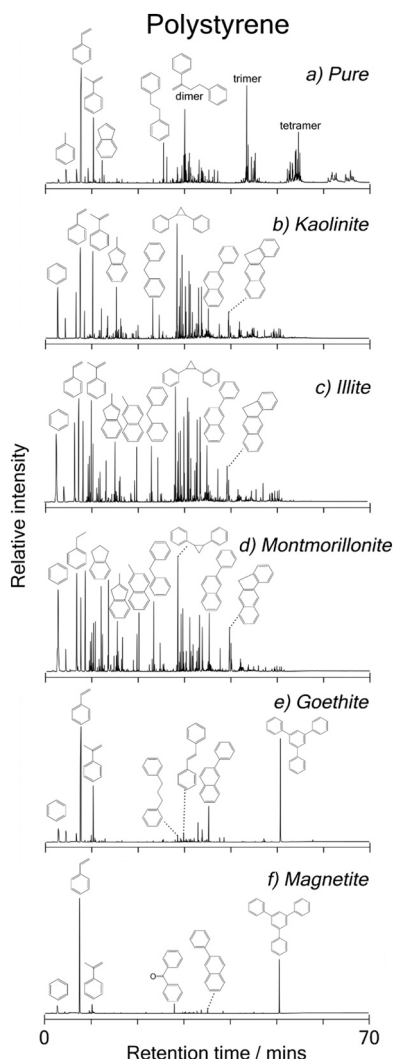


Fig. 3. Py-GC-MS total ion chromatograms of (a) polystyrene, and polystyrene (2 % w/w) mixed with (b) kaolinite, (c) illite, (d) montmorillonite, (e) goethite and (f) magnetite, all pyrolyzed at 650 °C.

them such as the larger relative intensity of methylnaphthalene in the PS with illite and PS with montmorillonite samples, and the larger intensity of ethylbenzene, ethyl-methyl-benzene and indene in the PS with montmorillonite sample. Similar results have previously been reported for PS mixed with illite [32].

In contrast to PS mixed with phyllosilicates, PS mixed with the iron oxyhydroxides/oxides, goethite and magnetite, generated quite different results, with pyrolysis products of both mixtures dominated by styrene and triphenylbenzene. Other molecules were detected at relatively low intensities including benzene, toluene, ethylbenzene, α -methylstyrene, and phenyl-naphthalenes. Stilbene (1,2-diphenylethene) and diphenylpropane were also detected from PS mixed with goethite. Interestingly, for PS mixed with magnetite several oxygen-containing molecules were detected including dibenzofuran, benzophenone and 9 H-fluoren-9-one.

3.4. Py-GC-MS of poly(vinyl chloride)

The pyrolysis products of PVC, shown in Fig. 4a, contained monocyclic and polycyclic aromatic hydrocarbons (PAHs). Benzene and naphthalene were the dominant peaks, however, toluene, styrene, indene, methyl-indene, methylnaphthalene, biphenyl, fluorene, acenaphthene and anthracene were also detected [38]. The TIC of the

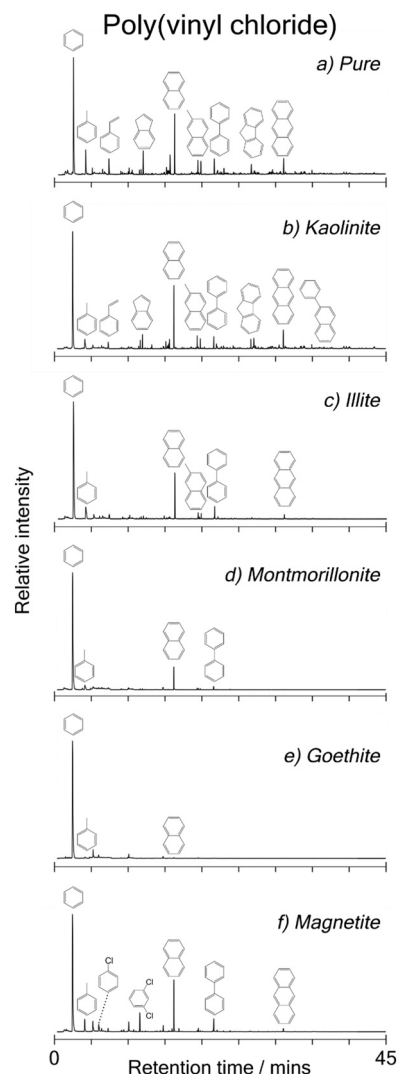


Fig. 4. Py-GC-MS total ion chromatograms of (a) poly(vinyl chloride), and poly (vinyl chloride) (2 % w/w) mixed with (b) kaolinite, (c) illite, (d) montmorillonite, (e) goethite and (f) magnetite, all pyrolyzed at 650 °C.

pyrolysates of PVC mixed with kaolinite, Fig. 4b, is very similar to PVC pyrolyzed alone, the same molecules were detected with only minor changes in the relative intensities. The other phyllosilicates analysed, illite and montmorillonite shown in Fig. 4c and d respectively, displayed more pronounced changes and reduced the TICs to benzene, toluene, naphthalene, methylnaphthalene, biphenyl and anthracene.

The addition of iron oxyhydroxides/oxides greatly affected the pyrolysis products of PVC, especially when mixed with goethite, Fig. 4e; a large signal was observed for benzene, but all the other molecules were reduced to very low relative intensities. PVC mixed with magnetite, shown in Fig. 4f, retained more of the original signal, with naphthalene, biphenyl and anthracene detected. Interestingly, chlorinated molecules were detected for PVC mixed with magnetite; these were mono-, di- and tri-chlorobenzene. Mechanisms for the formation of chlorinated and aromatic molecules are given by [39].

4. Discussion

In the results presented above we have shown how the mineral matrix can affect the Py-GC-MS response of a range of polymers. This can lead to interpretation errors when analysing plastics in different environments.

Several publications have summarised the characteristic molecules that could be used when trying to identify polymers in environmental samples [40,41]. A mixture of reference polymers were analysed using Py-GC-MS, with the following molecules used as representative compounds: 1,20-heneicosadiene for PE, 2,4-dimethyl-1-heptene for PP, styrene trimer (2,4,6-triphenyl-1-hexene) for PS, and naphthalene for PVC [42]. The same peaks were chosen by Fischer and Scholz-Böttcher when analysing environmental samples [43,44], however they used benzene as an indicator peak for PVC. 2,4-dimethyl-1-heptene was also chosen as a calibration peak for PP by Steinmetz et al. in their study on the quantification of plastic debris in soil, however styrene and α -methylstyrene were chosen as representative peaks for PS, and C₁₅, C₁₇ and C₁₈ alkadienes were chosen as calibration peaks for PP [45]. Similar peaks were also chosen by Dierkes et al. [46]. There are limitations to the compounds chosen in these studies to identify and quantify plastics in environmental samples, as the authors have tried to strike a balance between choosing a compound that is unique to the polymer, however, often this involves choosing a compound that may have a low abundance (and therefore lead to poor detection limits of the plastic), rather than an indicator compound that is dominant but not specific to the polymer. This is the case for PE, where alkadienes are often chosen as indicator peaks due to their specificity, however, they are often lower in intensity than alkanes and alkenes which could arise from a multitude of other materials.

Following our work, we now recognise that, when polymers are mixed with certain minerals, previously proposed monitoring methods may fail. In general, when the polymers analysed in this study are mixed with phyllosilicates, some of the representative peaks remain. However, in the presence of iron oxyhydroxides/oxides, the TICs are mostly unrecognisable from the original polymer. To add to this confusion, when some polymers are in a certain matrix, they may resemble other polymers; this is the case for PE mixed with magnetite (Fig. 1f) in which the same aromatic molecules were detected as PVC mixed with montmorillonite (Fig. 4d). Representative peaks of benzene and naphthalene could be used for PVC, however these are commonly detected in the other polymer-mineral combinations analysed in this study, and are non-specific peaks that could also arise from other sources. 2,4-dimethyl-1-heptene is a good choice of indicator peak for PP as it is specific to that polymer, however, it was only detected in pure PP and PP mixed with magnetite in our work.

There are some polymers analysed in this study which have peaks that could be unanimously used, such as styrene and α -methylstyrene in PS, which were present in PS regardless of the mineral composition. However, we also detected styrene in some samples containing PE and PVC. Other compounds, such as the styrene trimer which has been used as an indicator peak for PS in other studies [42–44], are much more specific and could only arise from PS. However, the styrene trimer is much less abundant than styrene, therefore using this as an indicator peak leads to poor detection limits. In our work, we only detect the styrene trimer in pure PS, therefore it is not a good indicator peak to use when analysing plastic pollution in soils.

Pyrolysis mechanisms for the polymers studied in this work are well known [45 and references therein], namely random scission, side chain scission and monomer reversion, but these are deviated from when minerals are present. The mineral assisted aromatisation of compounds, as observed in PE and PP, is likely formed from cyclisation and dehydrogenation reactions [47–50]. However, there are also complex mineral assisted reactions that differ substantially from the classical thermal dissociation products. With the effects of inorganic-organic interactions demonstrated using potential soil components, it should be recognised that soil pre-treatment steps (e.g. [51–54]) can either mitigate or promote such reactions by varying the relative abundance of potential reactants. The polymers detected when using density separation, which has been used to separate microplastics from soil samples, is dependent on the setup used with high-density solutions able to extract all polymer types, whereas low-density solutions are used for more targeted analyses

[52].

Quantitation of organic-inorganic reactions, in the context of our target material and components, is a future prospect that would require the use of internal standards.

5. Conclusions

Evidence for the detrimental effects of plastics in the environment is growing [14]. Any regulations associated with plastic contamination will require methods for the identification of non-compliance. Pyrolysis is an excellent and efficient technique for the environmental monitoring of plastic waste, yet its limitations need to be understood so that appropriate pre-treatment steps can be introduced to enable accurate identifications to take place. Our data reveal that when Py-GC-MS is performed in the presence of the common soil minerals phyllosilicates and iron oxyhydroxides/oxides, the distinctive polymer fingerprint may become obscured. We have documented the responses for the polymers, polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC) in the presence of phyllosilicate and iron oxyhydroxides/oxides minerals. The mineral-assisted transformations of plastic pollution is most dramatic for iron oxyhydroxides/oxides (goethite and magnetite). Our data suggest that the monitoring of plastic contamination in soils by Py-GC-MS should combine both mineral and organic analysis and that the resulting data be interpreted in the context of potential mineral-assisted organic reactions.

CRedit authorship contribution statement

Jonathan S. Watson: Writing – review & editing. **Mark A. Sephton:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Tara L. Salter:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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