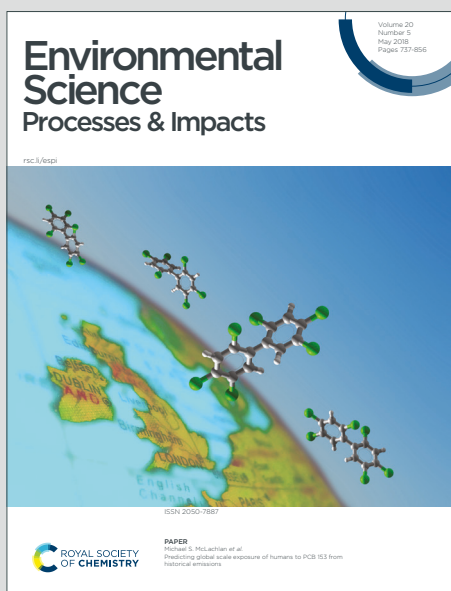


Environmental Science Processes & Impacts

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Environmental Significance Statement

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Plastic pollution is a worldwide issue of great environmental concern and is at the forefront of public concern. Once plastics enter the environment, the chemicals that leach out of them can affect the health of both wildlife and humans and can contaminate land and water. Despite this, there is still no standardised method for the sampling and characterisation of plastics. Developing such a method by first fingerprinting known plastic samples would allow the forensic analysis of environmental plastic samples, allowing the tracing of original polymers, original item types, manufacturing locations, and potentially even manufacturing companies. In turn, this could allow the reduction of plastic pollution through evidence-based litigation, regulation, and remediation.

Environmental Science: Processes & Impacts Accepted Manuscript

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Double-Anonymised Title Page

Authors:

D. J. Jones^a R. Francis^b S. J. Campbell^c I. D. V. Ingram^a R. Sühring^d H. Nguyen^d S. Potgieter-Vermaak^a and D. Megson^{a,e}

Affiliations:

a Manchester Metropolitan University, Manchester, England, United Kingdom

b Markes International Ltd., Bridgend, Wales, United Kingdom

c Spectral Works Ltd., Runcorn, England, United Kingdom

d Toronto Metropolitan University, Toronto, Ontario, Canada

e Chemistry Matters Inc., Calgary, Alberta, Canada

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Author contributions:

David J. Jones: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Visualization, Project administration.

Ryan Francis: Methodology, Investigation, Writing - Review & Editing.

Huy Nguyen: Software, Formal analysis, Data curation, Visualization.

Roxana Sühning: Validation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Ian D. V. Ingram: Validation, Writing - Review & Editing, Supervision.

Scott J. Campbell: Software, Writing - Review & Editing.

Sanja Potgieter-Vermaak: Supervision.

David Megson: Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.



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ARTICLE

The use of thermal desorption gas chromatography mass spectrometry (TD-GC-MS) to differentiate sources of plastic pollution

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Plastic pollution is an increasing global concern that has been shown to damage our environment. The current literature focuses on detecting the presence of plastic in environmental matrices, but little has been done to develop methods to identify the sources of plastic pollution. In this manuscript we present the use of thermal desorption gas chromatography mass spectrometry (TD-GC-MS) as a novel tool to undertake environmental forensics for plastics. Paired plastic samples were obtained from coastal waters and beaches in California and compared against store bought equivalents. Samples were processed into the microplastic size range (one to five millimetres) and analysed directly by TD-GC-MS. This research was able to identify unique marker features for four different polymers showing that bulk characterisation by TD-GC-MS is possible. The chemical fingerprint was then further interrogated to show how it is possible to identify specific marker features that differentiated the same polymer produced by different manufacturers. This was evidenced through examples with biaxially-oriented PET (differentiating Mylar from PET) and latex (differentiating producers from U.S.A. and China). This research demonstrates that environmental forensics for plastics is possible, and valuable diagnostic information can be gained from the chemical fingerprint. TD-GC-MS coupled with a statistically robust approach, and optionally as a complement to other techniques such as pyrolysis, offers a powerful tool for identifying the origins of pollution, allowing both a more complete understanding of plastic pollution, but also enabling its effective regulation.

achieve the required performance in its intended use, such as a specified lifetime for plastic window frames exposed to sunlight before the plastic becomes too degraded to be useful.⁷

Production chemicals are unintentionally left over after processing which then become contaminants, and can include catalysts, solvents, and process lubricants not completely removed from the final product. These can be present in commonly-found plastics.⁸

Unintended additional chemicals that were never intended to be part of the final polymer product can also be introduced before, during, or after manufacture. These might include by-products of manufacturing, degradation products, other contaminants such as dust and debris from a factory, or chemicals that the plastic picks up from the environment once in use or after being discarded.⁹⁻¹²

Large plastic particles can degrade to form micro and nanoplastics, which are more easily dispersed in the environment, and can form important pathways of exposure for biota.¹³⁻¹⁷ The chemicals present within a plastic can be considered as pollutants, as well as the plastic particle itself. Additives (and any other associated chemical payloads) present within these plastics can leach into the environment and affect wildlife and even human health,^{7, 18} and this has been identified as a planetary boundary threat in itself.¹ Additives and by-products have been shown to harm humans and animals via the same exposure routes. There is a large amount of data detailing the harm that plastics and additives exposure can do to multiple species of fish,¹⁹ but other animals can be affected too, such as

Introduction

The global scale of plastic pollution is now widely known and is regarded as a planetary boundary threat,¹ meaning that it has the potential to permanently destabilise key ecosystems. There is also evidence that plastic pollution can itself make other planetary boundary threats worse, including ecological, climate, atmospheric, and marine boundaries.^{2,3} However, many aspects of the impacts of plastic pollution on both human and animal health and the wider environment are still poorly understood.⁴ An important complicating factor is that many plastics contain, in addition to the base polymer, a wide variety of additives, contaminants, and other trace chemicals, including functional additives, production chemicals, or unintended additional chemicals. Functional additives are added for a purpose and give a polymer desired properties. Examples include UV stabilisers, plasticisers, antioxidants, flame retardants, oxygen scavengers, and dyes or pigments. These are intentionally added to many plastic items, often in quite large quantities with flexible PVC commonly comprising >50% additives by weight.⁶ These functional additives are often essential for the plastic to

^a <Author affiliations omitted for double-blind peer review>

[†] Footnotes relating to the title and/or authors should appear here.

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seabirds, in which bioaccumulation of plastic-derived chemicals has been identified.²⁰⁻²²

Another well-studied example of this is the additive 6PPD, which is a common antiozonant in vehicle tyres (an additive to prevent rubber degradation from ozone exposure).²³ Fine pieces of material break off a vehicle tyre as it wears, and the 6PPD then reacts with ozone in air to form 6PPD-quinone, which can leach out into the surrounding environment.^{19, 24} Rainwater can then wash this leachate into drains, and subsequently into rivers and oceans, where it has been seen to affect salmon in both North America and Australia, demonstrating that additive pollution is a worldwide problem.^{19, 24-26}

Additives that are found to be harmful are often subject to regulations that either reduce or ban their use. For example, use of the once-ubiquitous plasticiser diethylhexyl phthalate (usually abbreviated to dioctyl phthalate, DOP) has been restricted in the European Union since its metabolites were shown to act as endocrine disruptors.^{27, 28} These regulatory changes provide an opportunity to ascertain the age and manufacturing location of a plastic sample; as additives are banned at specific points in time in specific regions of the world, there are only certain time periods in which specific additives are likely to have been used. The presence of specific additives in a plastic therefore gives an indication of when and where an item was manufactured. This, in combination with an understanding of which additives are characteristic of not only a particular plastic, but a formulation of that plastic for a particular intended product or use, offers the possibility that analysis of the additive (and possibly use-specific contaminant) “fingerprint” of microplastic and plastic samples will reveal details of their age, origin, and the original product from which they have fragmented. Crucially, this would lead to specific and granular origin, function, and time-dependent information via an analysis primarily of lower molecular weight species found alongside the primary polymer(s).

Analysis of plastic in the environment is predominantly undertaken using microscopic and spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. These techniques can identify the polymer, but they cannot split the plastic into its separate features such as the polymer and additives – the ability of TD-GC-MS to do this is what makes it possible to ‘fingerprint’ a plastic through the specific combination of chemicals within. Pyrolysis-gas chromatography with mass spectrometry (Py-GC-MS) is a technique that is gaining popularity for plastic analysis. However, by its nature this technique degrades the plastic at high temperatures of up to 600°C,²⁹ meaning that it is often the degradation products of the plastic that are being analysed rather than the plastic itself. Thermal desorption gas chromatography mass spectrometry (TD-GC-MS, or simply TD when describing just the thermal desorption instrument itself) is a relatively underutilised technique for plastic analysis, and makes an excellent complementary technique to pyrolysis. While pyrolysis uses high-temperature combustion, TD works by heating the sample gradually and less aggressively than this and to a lower maximum temperature of around 300°C, beyond which most polymers begin to break down. Although some

degradation will still occur with any form of heating, TD tends to retain potentially larger biomarkers and potentially more biomarkers than can be analysed with just pyrolysis alone. As larger biomarkers occur less commonly, they tend to be more diagnostic, making diagnostics simpler and more powerful. TD-GC-MS can also be used as a standalone technique.

Overall, all this offers significant promise for the forensic analysis of plastic particles, and subsequently microplastic particles in terms of their detailed chemical payload of additives, contaminants, and leftovers from production.

This work aims to investigate the use of TD-GC-MS as an environmental forensic tool for plastic pollution to attempt to differentiate polymer types, product or processing classes, manufacturing location, and between paired environmental and store-bought samples.

Materials and Methods

Sample selection and preparation

A combination of environmental and store-bought samples were obtained, referred to as ‘macro-samples’ as they were split into smaller samples in the lab. Five ‘environmental’ macro-samples (Table S1) were collected from coastal waters and beaches in California by citizen science partners conducting litter clean-ups during annual California Coastal Clean Up Day events. Fourteen ‘store-bought’ macro-samples (Table S2) were purchased by the California State Water Resources Control Board (California SWRCB) and then mailed to the UK. For both macro-sample categories, macro-samples were selected to include the most commonly-found plastic items during the aforementioned Clean Up Day events from 1988 to 2020, and all the collected macro-samples were macroplastics – items that were large enough for the product itself to be identifiable – to allow analogous store-bought samples to be purchased. Each environmental macro-sample had a paired store-bought equivalent (Table S1). Across both environmental and store-bought samples, types of sample included latex and Mylar balloons, cups, cutlery, drinking straws, bottles, and bottle caps. Details of all samples can be found in Tables S1 and S2.

Sample preparation was conducted in accordance with Markes International Application Note 161.³⁰ Fragments were cut from the macroplastic samples into microplastic-sized pieces (longest dimension between one and five millimetres), then individual pieces were trimmed to a mass of approximately one milligram using stainless steel scissors to create the final TD samples. In tables S1 and S2, these are the ‘samples’ – subsamples of the macro-samples. All samples were handled using ceramic-tipped tweezers. Both the scissors and the tweezers were cleaned with acetone on a clean wipe tissue before, between, and after handling samples. Neoprene gloves were used throughout to prevent skin oil contamination. Samples were homogenised and weighed out using a micro-balance. Three 1 ± 0.0001 mg replicates were taken from each macro-sample, for a total of fifteen environmental samples and forty-two store-bought samples.

Samples were stored in out-of-the-box amber glass vials until the empty stainless steel TD sample tubes could be conditioned by heating them for four hours to 400°C in a 100 mL min⁻¹ flow of nitrogen using a Markes International TC-20 TD tube conditioning instrument. Quartz fibre filter paper discs (47 mm diameter, Cytiva Whatman™ via Fisher Scientific) were cut into quarters using the stainless steel scissors, wrapped in aluminium foil and conditioned at 500°C in a ceramic brick lined furnace overnight. Each sample was then wrapped in a quarter of a filter paper disc by hand while wearing the neoprene gloves. The wrapped sample was then inserted into the sample tube using a Markes TubeMate™ tool (Markes International), which was marked to ensure a consistent and reproducible insertion depth within each TD sample tube.

FTIR was performed on a selection of known plastic samples to confirm that the system of using the resin identification code (RIC) to identify the polymer of a store-bought plastic was indeed plausible.

Instrumental analysis

Analysis was performed using a Markes International TD-100xr TD instrument integrated with an Agilent 8890 GC system and coupled with an Agilent 5977B GC/MSD MS system. The internal standard (IS) used was toluene-D8, which was introduced into the instrument and run alongside all samples, including all 156 sample and instrument blanks. A focussing trap was used to pre-concentrate the VOCs emitted from the plastic samples and enable injection onto the GC in a narrow vapour band. The TD instrument was configured with a flow path temperature of 250°C, with a 12 min split sample desorb at 320°C, a trap flow of 20 mL·min⁻¹ and a split flow of 80 mL·min⁻¹. The trap desorb time was 10 min with a maximum temperature of 320°C, a desorb split flow of 30 mL·min⁻¹, and a 1 min purge (25°C, 50 mL·min⁻¹). The carrier gas used was helium with a GC run time of 30 min with an additional 2 min post-run. The column was an Agilent Zebron ZB-35HT Inferno (dimensions 30 m x 250 µm x 1.4 µm, flow rate of 1.5 mL·min⁻¹). A starting temperature of 40°C was used, with a ramp between 10 and 30 min of 15°C·min⁻¹, a hold time of 6 min at 250°C, and a post-run temperature of 200°C. The MS was configured to scan from *m/z* 34 to 350. Since all macro-samples were split into three fragments (samples), this meant that all macro-samples were run in triplicate. One blank sample tube was analysed between each replicate to assess carryover.

Data Analysis

Initial data analysis was performed using MassHunter Workstation Software Qualitative Analysis (version B.07.00, Agilent Technologies). Detailed data analysis, including automated integration and statistical analysis, was performed using AnalyzerPro® XD (SpectralWorks). This software was used to compare spectra, to produce volcano plots at a confidence level of *p* = 0.05, and to produce and export feature response data tables for groups of analysed samples. Data normalisation and principal component analysis (PCA) were performed using

RStudio (version 2023.06.0) using packages “factoextra” and “FactoMineR”. For this, the GC spectra were cleaned by applying blank correction and a minimum signal threshold, and negative or zero values were changed to a very small value to avoid calculation errors when dividing. In addition, any features only found in one sample in a set were removed. Normalisation was calculated by summing the total area of all peaks in the total ion chromatogram and then dividing the area of the peak being investigated by this total, giving a value for the peak as a decimal fraction of the total area. Any further analysis was then done using the cleaned, normalised, blank corrected data. Further information on data cleaning and normalisation can be found in the supplementary information of the relevant referenced literature.^{31,32} For data analysis purposes, all of the environmental samples were grouped together in a category of their own, and the store-bought samples were individually labelled with their polymer type, determined by a combination of information from the item’s resin identification code (RIC), the package labelling, and evidence for what individual items are expected to be made from (for example, plastic drinking straws were labelled as polypropylene (PP) unless the packaging stated otherwise, as PP is the most common material for this item).³³ Identified features were matched to chemical compound names using the NIST Mass Spectral Library, which matched features based on retention time.

It is important to note that the primary goal of this analysis was to differentiate different polymer types, manufacturing origins, and environmental vs store-bought samples, rather than to identify and characterise individual features to the highest confidence levels. All feature and compound assignments within this manuscript are therefore putative.

Quality Assurance

A total of 156 blanks (empty TD tubes) were run during the TD analysis, with at least one blank run between each sample, to ensure minimal carry-over. In the lab, samples were handled using neoprene gloves to avoid skin oil contamination and were stored in a cardboard box to avoid contact with any other plastics. All blanks were assessed for carry-over and contamination. Limited carryover was identified in some blanks along with siloxanes originating from the GC column. The PCA analysis was conducted based on blank-subtracted peak areas. For the remaining analyses no blank subtractions were performed, since no features that were identified as diagnostic markers for any sample type were identified in the blanks.

Results and Discussion

Six different polymer types were identified from the store-bought samples: natural rubber latex (latex, 6 samples); metallised Mylar (9 samples); polyethylene terephthalate (PET, 3 samples); polylactic acid (PLA, 3 samples); polypropylene (PP, 3 samples); polystyrene (PS, 18 samples). Although Mylar is a brand name of biaxially-oriented PET (boPET), the name Mylar has been used in this study because it was stated on the packaging of the samples used, and different brands of boPET

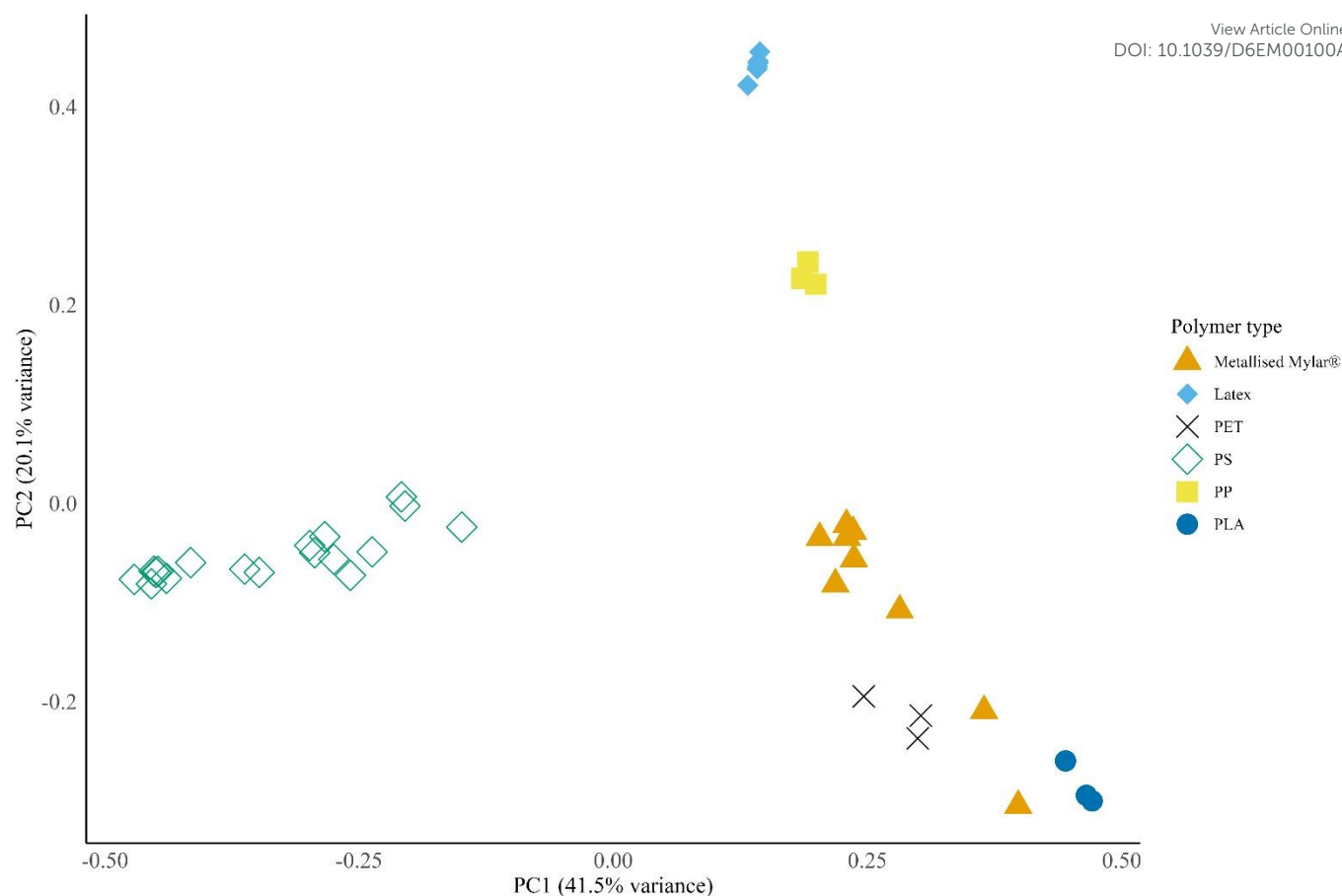


Figure 1: PCA scores plot for all 42 store-bought samples, showing a separation of the latex, PP, and PS samples from Mylar, PET, and PLA.

may differ in composition. Hence, the results of this study apply to Mylar specifically.

In the differentiation of polymer types, a total of 231 unique potential marker features were identified. PLA had the greatest number of these at 121, whereas PS had the fewest at two. A pairwise comparison between only metallised Mylar and PET revealed three unique potential marker features; two for metallised Mylar and one for PET.

In the differentiation of manufacturing origins, a total of thirty-six unique potential marker features were identified; twenty-two for samples made in the U.S.A., and fourteen for samples made in China.

For the comparison of environmental samples vs store-bought samples, groupings were arranged by item type, and twenty-five unique potential marker features were identified that were present in the environmental samples and not in their paired store-bought equivalents; one for balloons, two for plastic bottles, sixteen for plastic cups, and six for plastic drinking straws. Additionally, six unique potential marker features were identified that were present only in the store-bought items and not in their paired environmental equivalents; one for plastic drinking straws and five for plastic bottle caps.

Differentiation of polymer types

Samples were initially grouped by their polymer type, and principal components analysis (PCA) on the TD-GC-MS data was used to identify any differentiable clusters of samples, which would indicate unique chemical signatures. The PCA showed three distinct clusters for latex, PS, and PP (Figure 1) indicating that these polymer types had significantly different chemical signatures.

However, there was a large degree of overlap between the remaining polymer types (metallised Mylar, PS, and PP). This was not surprising, considering that polymers contain large numbers of short chain hydrocarbons, such as CH_2 groups, that could have overwhelmed the potential contributions of other chemical groups in the PCA.

PCA was therefore clearly not suitable for detecting more subtle differences such as differences in the chemical fingerprint based on the manufacturing location. To derive detailed chemical fingerprints that would allow for such differentiations, we investigated whether the presence of unique potential marker features could be a better approach to distinguish the different polymers.

To accomplish this, a univariate method was used where volcano plots were generated to visually identify unique chemical features for a given group of samples that were not seen in other samples. An iterative approach was used whereby all samples of interest (e.g. of a specific polymer type) were grouped and compared against a single other group containing

all other samples, and this was then repeated for each set of samples to be investigated.

More detailed analysis was then undertaken from the feature response data table, which comprised response areas for each detected feature for every sample. Features that were present in every sample from the sample group of interest, but absent from all other samples, were unique potential marker features for that specific sample group of interest. The identified unique potential marker features were then ranked based on their average instrument response, with a greater average response being ranked as better. The confidence interval of $p = 0.05$ was only used when visually identifying whether any unique features were present at all. Since the actual feature identification was done through the feature area response data table using a binary filter, no adjustment was needed for multiple testing; features were classified as either present in the sample group of interest and not in anything else, or not counted. As an example, the volcano plot generated for latex (Figure 2) showed a great number of significant chemical features for latex, many of which are above the $p = 0.05$ confidence line. This gave an early visual indication that unique potential marker features for latex were present. Looking at the feature area response data table,

eighty-seven unique chemical features were identified that were present in all latex samples and none of the other samples (i.e. therefore not in any of the other polymer types, Table S3). The unique potential marker feature for latex with the greatest area response was tentatively identified as 2-(4,8,12-trimethylcyclotetradeca-3,7,11-trien-1-yl)propan-2-ol, which was present with a high peak area in all latex samples (mean area 2.5×10^7 across all latex samples) but was not present in any other analysed polymer type (i.e. not in any other sample).

PP), as well as a fourth polymer type that the PCA was not able to distinguish (PLA). Using the univariate approach, unique potential marker features were identified for PLA (121 unique potential marker features), latex (87), PP (21), and PS (2). These unique potential marker features are summarised in Tables S3-S6. The only two polymer types for which no unique potential marker features were identified were metallised Mylar and PET, indicating high chemical similarity between these polymer types and the other analysed polymers. Furthermore, the chosen analytical technique does not provide information on inorganics such as trace-metals, therefore other analytical or data analysis techniques would need to be employed to distinguish non-metallised Mylar and metallised Mylar. For the latex samples, the selected unique potential marker features could be explained by the polymer; rubber usually consists of a polyisoprene, and the identified markers (Table S3) shared the same structural motif, which indicates that they likely arise either from main chain decomposition, or from the volatilisation of low molecular weight oligomers from the rubber matrix.

The unique potential marker features identified for PLA (Table S4) were possible fragmentation or decomposition products of the monomer. For PS, the identification of ethylbenzene (Table S6) can be explained as a styrene derivative.

The other unique potential marker features identified across the polymer types (Tables S3-S6) could not be traced directly to the monomer or known additives, but nevertheless, all identified unique potential marker features were statistically significantly present ($p < 0.05$). This method does therefore provide a process for identifying unique potential marker features from plastics via TD-GC-MS.

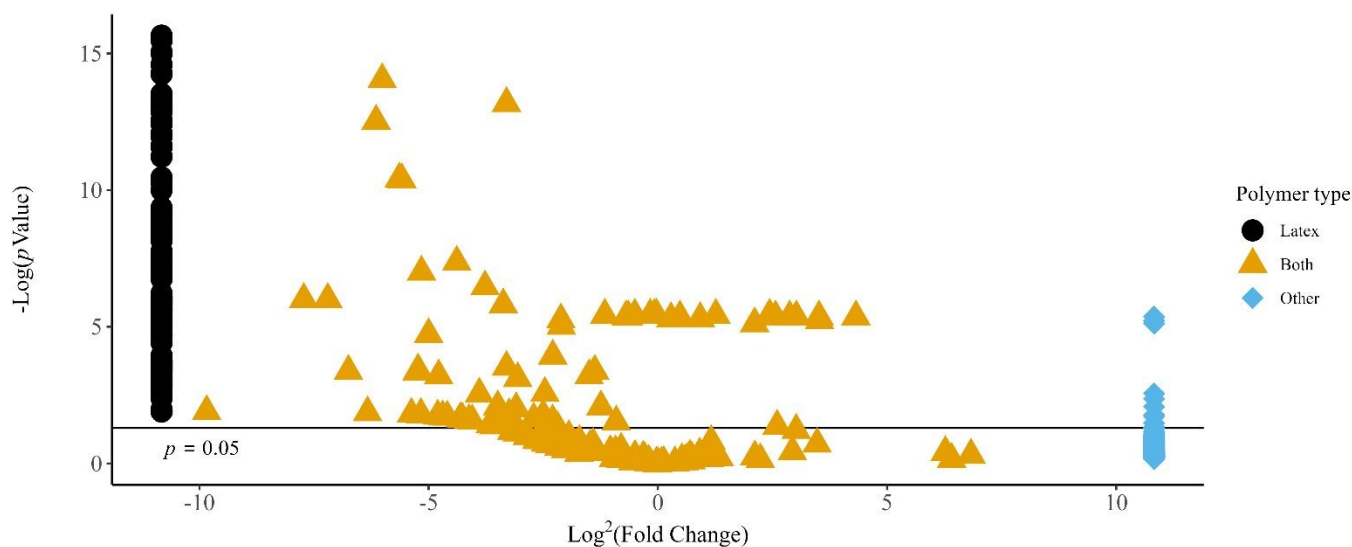


Figure 2: Volcano plot for latex vs all other samples, showing many identified statistically significant chemical features for latex (black circles), which could be potential marker features. Features unique to latex are represented by the black circles, orange triangles represent features present in both groups of samples, and blue diamonds represent features only present in other (i.e. non-latex) samples.

This univariate approach proved successful and highly complementary to the polymer differentiation based on PCA, as unique potential marker features were observed for all of the polymer types that PCA was also able to distinguish (latex, PS,

To further investigate the potential application of this method to identify unique potential marker features for the differentiation of polymer types, metallised Mylar and PET were assessed as an isolated pair with the univariate approach. To



investigate whether these two forms of the same polymer type could be differentiated from one another, the metallised Mylar samples were compared directly to the PET samples. Two unique potential marker features were found for metallised Mylar when compared to PET, and one unique potential marker feature was found for PET when compared to metallised Mylar (Table S7). This highlights the potential forensic applications to perform detailed source identification of plastics in the environment by using TD-GC-MS, even between different forms of the same polymer. In this case, differentiation was likely possible due to the subtle chemical signature left by the metallisation process, which was distinguishable by this technique despite the bulk polymer being PET in either case. The metallisation process can use methods such as vacuum metallisation or chemical-based methods such as mixing the metal into a complex (for example, a metal-phosphine complex) which is then evaporated onto the polymer surface^{34, 35} Whether this signature arose through heating during metal evaporation, or the use of an adhesion/sealant layer (usually very thin polyolefin layers) was not immediately clear.

Manufacturing Origin

latex as we possessed paired triplicated samples prepared in the U.S.A. and China, according to product packaging. Different origins of latex were indistinguishable in the PCA scores plot of all store-bought samples (Figure 1). However, the wide spread of the latex cluster along dimension 1 indicated a lot of variability in the chemical signature of the latex cluster, indicating potential for differentiation. Therefore, the latex samples produced in the U.S.A. (three samples) were compared directly to those produced in China (three samples) using another pairwise comparison with univariate approach (Figure 3), in the same way that Mylar and PET were directly compared. Details of the samples compared can be found in Table S2 within the latex balloon samples. Interestingly, there were twenty-two unique potential marker features identified for U.S.A. samples that were not seen in any of the China samples (Table S8), and there were fourteen unique potential marker features identified for China samples that were not seen in any of the U.S.A. samples (Table S9).

Nine of the twenty-two features identified as unique to the U.S.A. are benzene derivatives, which tend to result from the degradation of rubber,³⁶ and all the features identified for the U.S.A. items are structurally simpler molecules compared to

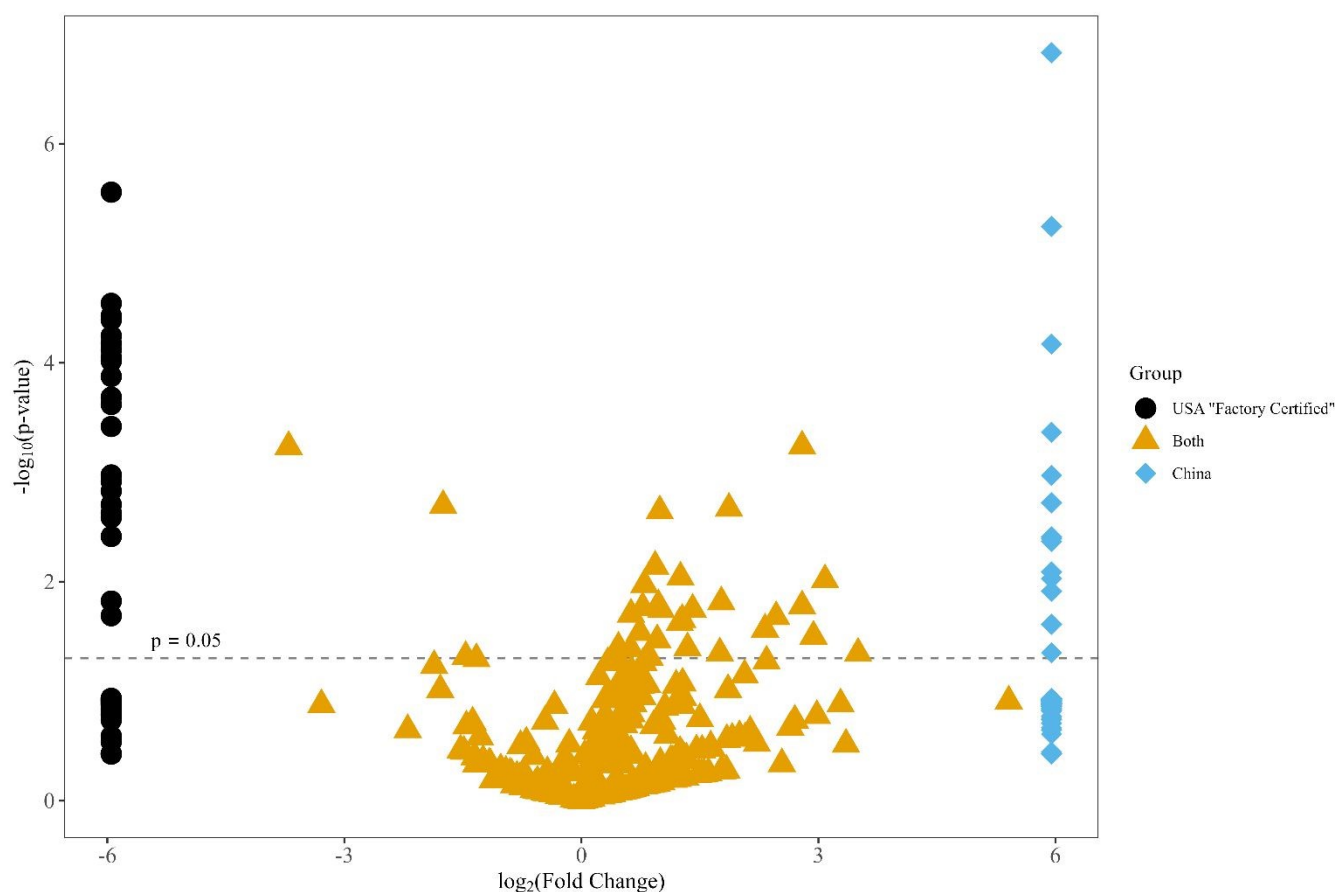


Figure 3: Volcano plot comparing samples manufactured in the USA (under a "Factory Certified" label) and those manufactured in China. The vertical columns on the left and right sides show a significant number of features unique to either the USA "Factory Certified" samples or the China samples, respectively. Features unique to samples made the USA are represented by the black circles, orange triangles represent features present to some degree in both groups of samples, and blue diamonds represent features unique to samples made in China.

The second aim of the study focused on differentiating items by their manufacturing origins. For this application we focused on those identified for China, in which there were only three



benzene derivatives out of a total of fourteen identified features.

This demonstrates the ability of our method using TD-GC-MS in conjunction with appropriate statistical methods to differentiate between samples of the same polymer type that are manufactured in different locations, although it is impossible to say whether these differences are diagnostic of manufacturing in those countries, the source of the natural latex itself, or the particular factories from this sample set. For this reason, further research is merited with a larger sample set.

Environmental vs Store-Bought Samples

The final aim of the study focused on comparing equivalent pairs of store-bought and environmental samples, paired by item type and polymer. The item types included were balloons, plastic bottles, plastic bottle caps, plastic cups, and plastic drinking straws. The environmental plastic bottle caps were paired with PP store-bought plastic drinking straws as they were made from the same polymer, and there was an absence of store-bought plastic bottle cap samples. Nevertheless, this still fulfils the requirement of an equivalent sample. Details of the environmental samples and their paired store-bought samples are available in Table S1, details of all the store-bought samples are available in Table S2, and details of the features identified during environmental vs store-bought comparisons are available in Tables S10 and S11.

Balloons: Three environmental balloon samples were compared against six latex and nine metallised Mylar balloon store-bought samples. Since the environmental balloon samples appeared similar to the store-bought metallised Mylar balloons, it was likely that they were made from the same polymer. To confirm this, a PCA scores plot with all the environmental and store-bought balloon samples was constructed (Figure S1). The environmental balloon samples clustered only with store-bought metallised Mylar balloon samples, and not with any other store-bought balloons of any other material. This indicated that the environmental balloon samples were likely very chemically similar to metallised Mylar, and were therefore likely made from the same material.

Using the univariate approach, one unique feature – tentatively identified as 1,6-dichloro-1,5-cyclooctadiene – was observed in the environmental balloon samples, but was not observed in any of the store-bought balloon samples, whether latex or metallised Mylar. The compound 1,6-dichloro-1,5-cyclooctadiene is a catalyst precursor used in the formation of metal complexes which could be used in the metallisation process. However, it did not appear in the list of identified unique potential polymer marker features, indicating that it was possibly created or added during environmental exposure or degradation of the material. More details on this compound can be found in Table S10.

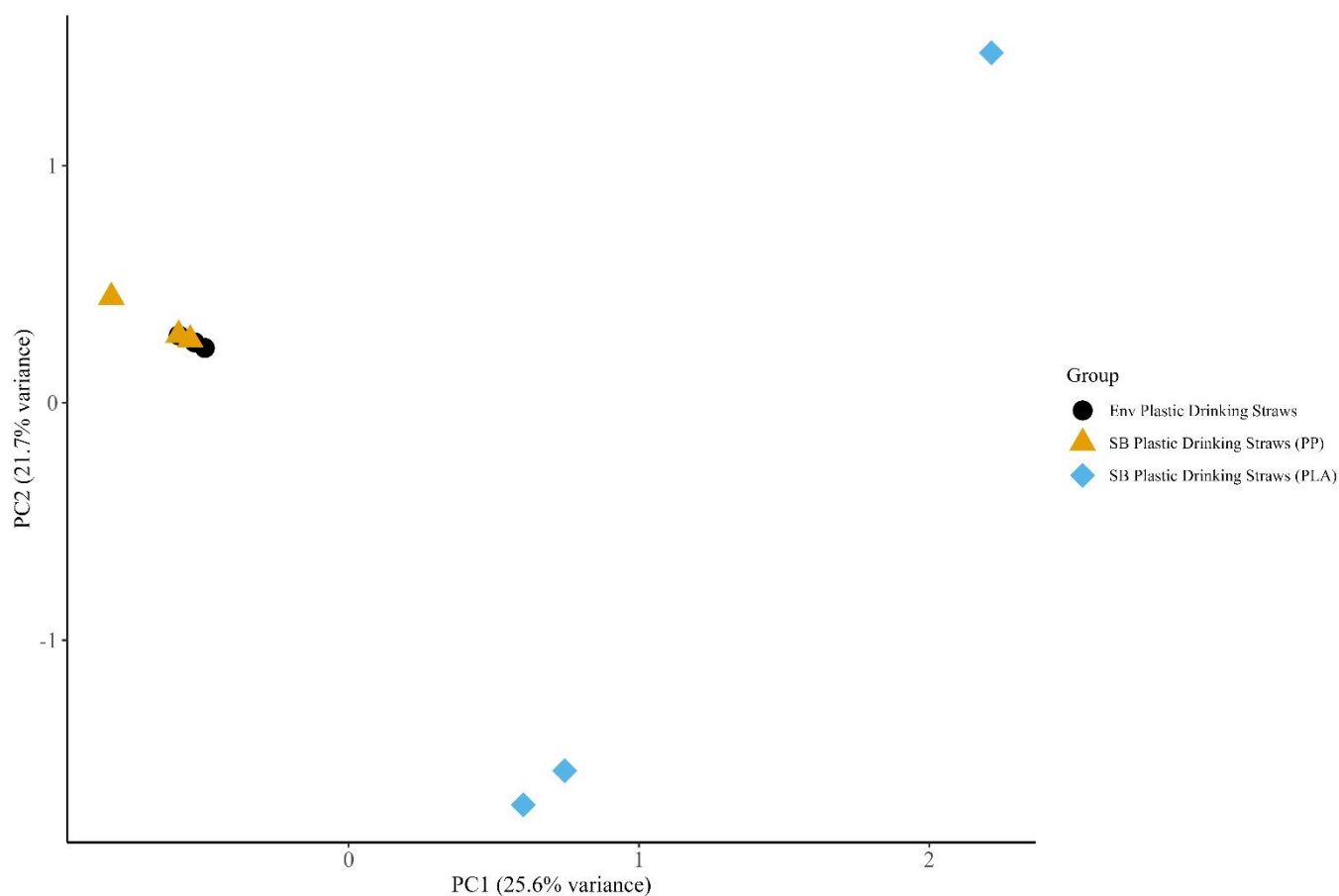


Figure 4: PCA scores plot for environmental plastic drinking straws vs store-bought plastic drinking straws of both PP and PLA polymer types, showing strong clustering of the environmental samples with the PP store-bought samples only.

Further research is warranted to investigate whether this compound was a residue from the metallisation process, or if it can be formed during environmental weathering of metallised Mylar.

Plastic bottles: Three environmental plastic beverage bottle samples were compared against three store-bought PET plastic bottle samples. Given their identical purposes, these items were likely to be made from the same polymer. Two unique features were found in the environmental samples that did not appear in any of the store-bought samples (Table S10). Both of these unique features (tentatively identified as 5-methyl-2-furancarboxaldehyde and (E)-cinnamaldehyde) are used as flavouring agents, indicating that they might have originated from the beverages stored in the bottles.

Plastic bottle caps: A distinction was drawn between plastic bottles (usually made from PET) and their caps (usually made from PP) due to the different polymer. As mentioned earlier, environmental plastic bottle caps were compared with store-bought PP plastic drinking straws as they are both made from PP. In this comparison, three environmental plastic bottle cap samples were compared against three store-bought PP plastic drinking straw samples, and five features were identified that were unique to the store-bought PP drinking straw samples (Table S11). These features may have leached into the environment and hence they are not present in the environmental plastic bottle cap samples, although it is hard to say this for sure due to the lack of store-bought plastic bottle caps available for a like-for-like comparison between environmental and store-bought bottle caps.

Plastic cups: Three environmental plastic cup samples were compared against eighteen store-bought plastic cup samples of varying types and colours, but all made from PS. On a PCA scores plot where the environmental plastic cup samples were compared to the store-bought plastic cup samples, a good level of separation on both the PC1 and PC2 axes was seen (Figure S2). This separate clustering between environmental and store-bought plastic cup samples indicated that the chemical composition of the plastic cups likely changed when exposed to the environment. Moreover, sixteen unique features were identified that were unique to the environmental plastic cups samples that were not present in the store-bought plastic cups samples (Table S10).

Plastic drinking straws: Three environmental plastic drinking straw samples were compared against six store-bought plastic drinking straw samples, including three made from PP and three made from PLA. This allowed a determination of material to be conducted for the environmental plastic drinking straw samples - it was expected these would be made from the most common plastic drinking straw material which is PP,³⁷ but PLA is another material that is sometimes used.

To investigate this, a PCA scores plot was produced to compare the environmental plastic drinking straw samples to the store-bought plastic drinking straw samples, including both PLA and PP store-bought samples (Figure 4). The PLA store-bought samples clustered away from all other samples, and the environmental plastic drinking straws clustered strongly with

the PP samples, indicating that the environmental samples were likely made from PP, not PLA.

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Since the material of the store-bought plastic drinking straws was then known, it was expected that some matches between the identified unique features in the environmental plastic drinking straw samples and the list of unique potential polymer markers identified from the store-bought plastic drinking straw samples would be seen. When these were compared using the univariate approach, six features unique to the environmental samples were found, which were not seen in any of the store-bought plastic drinking straws samples, whether made from PP or PLA (Table S10). One compound (tentatively identified as tridecane) was seen both in the environmental plastic drinking straws in this comparison between environmental and store-bought plastic drinking straws, and in store-bought PP plastic drinking straws in the comparison between environmental plastic bottle caps and store-bought PP plastic drinking straws, but at different retention times. It's therefore likely that these two compounds are different, but the NIST compound database identified tridecane as the closest match in both cases. Therefore, it is most likely that in this comparison between environmental and store-bought plastic drinking straws, one unique compound (the aforementioned tentatively-identified compound tridecane) was identified for the environmental plastic drinking straw samples. This compound may have been created or added when these samples were in the environment, or may be indicative of a historical additive no longer present in, or a process not applied to, the store-bought straws, given that the age of environmental samples is unknown.

One feature unique to the store-bought plastic drinking straws versus their environmental equivalents was identified, tentatively identified as diethylcyanamide (Table S11) – as this feature was not seen in the environmental drinking straws, this chemical may have leached into the environment from the environmental samples.

Future applications and limitations

This study has highlighted the potential applicability of TD-GC-MS to be used to undertake environmental forensics for plastics. Mass spectrometric methods to determine plastics predominantly use pyrolysis (Py-GC-MS) which heats the plastics to high temperatures to measure diagnostic fragments. The findings of this paper are important because the majority of literature appears to focus on pyrolysis only, but thermal desorption is an excellent complementary method to pyrolysis and has potential as a further diagnostic tool. TD can identify not only common polymer fragments and additives as pyrolysis can, but also potentially larger biomarkers and more biomarkers than pyrolysis, owing to the less aggressive heating method of TD. This is useful as larger biomarkers tend to be much less common and therefore more diagnostic.

Analysis of different products showed that it was possible to differentiate plastics based on polymer type with TD-GC-MS. With further method development the same quantitative

procedures used to provide quantitative analysis via py-GC-MS could be applied to TD-GC-MS for routine analysis of complex microplastics samples. The method also demonstrated how TD-GC-MS can help identify potential environmental damage, particularly for the identification of specific pollutants against whose products the collected plastics samples can be compared.

The unique feature for environmental plastic cups with the largest average peak area was tentatively identified as 4-methylheptane - a compound that is potentially fatal if swallowed or if it gets into an animal's airway (including humans) due to its poisonous nature.³⁸ The identified compound 4-methylheptane is a decomposition product of PP and hence is consistent with environmental degradation,³⁹ but may have otherwise arisen from sample exposure to fuels, as this compound is also found in petrol.⁴⁰ This demonstrates the harmful nature of some of the features present in environmental microplastic pollution. The ability to not only identify what a plastic fragment is, but the chemicals within it, can aid future environmental risk assessments.

The ability of our TD-GC-MS method to produce a more comprehensive analysis of the plastic chemical fingerprint than other methods (such as Py-GC-MS) creates the possibility for detailed forensic studies that can be used to identify sources of plastics and microplastics, and reveal more about their fate and transport. This may also be applicable to the emerging field of nanoplastics, as TD-GC-MS can analyse extremely small fragments.

We were also able to identify specific marker features that differentiated the same polymer produced by different manufacturers. This was evidenced through examples with biaxially-oriented PET (differentiating Mylar from PET) and latex (differentiating producers from U.S.A. and China). This method allows us to monitor the changes in the chemical signature of samples, which could be due to degradation of the plastic material, or due to accumulation of other chemicals as the plastic acts like a passive sampler picking up other chemicals in the environment. TD-GC-MS would be a powerful tool to be used with lab and field based controlled experiments to analyse the chemical signature of samples, their origin, and their history. This TD-GC-MS-based method, both in standalone and complementary forms, should be further explored to investigate whether the additive signatures can be used to determine or differentiate different sources (such as plastic products). The key advantage of TD-GC-MS over other methods is that with TD-GC-MS, extra information about the sample is preserved within the data.

We acknowledge several limitations of this research. It was not intended to identify and characterise individual features to the highest confidence levels but instead to provide the first proof of concept for micro analysis of plastic particles as part of plastic environmental forensics, which can lead directly to microplastic environmental forensics in future research. To build on this work we would recommend further research that utilises high resolution mass spectrometry and analytical standards for confirmatory analysis of unique marker features,

including the use of TD-GC-MS in both a standalone form and as a complementary method to techniques such as pyrolysis.

Whilst every effort was made to link environmental samples with store-bought equivalents, we accept these are unlikely to be direct matches. It is therefore not clear where the unique features in environmental samples arose from (e.g. different manufacturing additives, degradation products, or environmental accumulation). What is important is that our method showed that they were different - this shows the potential of these chemical fingerprinting techniques. In addition, we did not analyse all polymers or plastic products ever produced. Therefore, whilst marker features were unique to our study they may not be unique in all cases, but the features we identified were highly diagnostic and so likely to be of use in future investigations. Nevertheless, we recommend future studies follow our workflow to identify their own unique marker features on a case-by-case basis, as these are likely to differ depending on the specific scenario.

Conclusions

Here we present the first use of thermal-desorption-GC-MS for chemical fingerprinting of plastics. The results show that when paired with an appropriate statistical analysis method, it is a powerful tool for the analysis of environmental plastics; this technique can readily distinguish environmental from non-environmental samples, it can be used to differentiate manufacturing origins for the same polymer, and it can also differentiate between nearly identical plastic materials such as PET and metallised Mylar. This offers a powerful methodology for detailed chemical fingerprinting of environmental plastic fragments which allows maximum information to be gathered about their origin and to some extent their history.

With this methodology, thermal desorption can also be employed as an excellent complementary method to pyrolysis, as thermal desorption has the ability to potentially retain larger biomarkers, making diagnostics simpler and more powerful.

Plastic pollution is now widespread and firmly in the public consciousness, but there is currently no widely adopted way to track the origins of plastic pollution. This technique demonstrates an effective solution by using chemical signatures to provide diagnostic information on the source of plastic pollution. This research could enable a new world of informed regulation and legislation, as it is possible to track plastic pollution back to manufacturers. This detail will be incredibly valuable in understanding and modelling plastic pollution, an essential step towards effective regulation and mitigation of this globally critically urgent problem.

Author contributions

<Author contributions omitted for double-blind peer review>

Conflicts of interest

There are no conflicts to declare.



Data availability

The data supporting this article have been included as part of the Supplementary Information.

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The data supporting this article have been included as part of the Supplementary Information.

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