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Towards a model for road runoff infiltration management

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In human society, there is a demand for sustainable solutions for water preservation and efficient treatment systems. An important water reservoir is road runoff defined as rainwater leaching from roads, loading micropollutants and infiltrating the soil. We aimed to study this poorly understood feature using large-scale metabolomic analysis coupled with analysis of soil physico-chemical properties and molecular chemical similarity enrichment. A total of 2406 micropollutants were assayed to understand their distribution and assess the trapping abilities of a road runoff infiltration system composed of a sedimentation pond and an infiltration pond. Here, we confirm the essential role of the infiltration pond in preventing environmental contamination and propose a model correlating micropollutant abundance and the soil physico-chemical properties. We demonstrate that sand in infiltration ponds is a key player, helping retain 86% of the micropollutant abundance and propose a model that could be easily applied for road runoff management.

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INTRODUCTION

The preservation of water resources is a pressing concern. Road runoff is a non-negligible water input originating from the leaching of roads by rainwater. Little attention has been given to the micropollutants in road runoff and their contribution to environmental pollution. Road runoff can carry fuel, oils, brake fluids, tyre particles, de-icing agents and other pollutants that contain heavy metals, polycyclic aromatic hydrocarbons (PAHs), salts, microplastics, particles, etc.^{1–4}. Phytosanitary products used for road management are also washed off by rain and can reach groundwater as already demonstrated in the case of urban wastewater⁵. The collection and storage of road runoff water prevent the spread of pollutants to surrounding areas and the erosion of banks. Worldwide, underground infiltration⁶, porous pavements, direct infiltration, rain gardens, bioswales and wetlands⁷ are used. Sometimes runoff water is collected for reuse⁸, but knowledge about its chemical and molecular content is increasing and these waters have been recognized as being harmful to humans and to the environment⁹ and need to be collected and managed as close to their source as possible.

One way to manage the collected water is infiltration, which allows groundwater recharge and reduces peak flows and volumes when the collected water is infiltrated near its collection point^{10,11}. Infiltration of potentially polluted water raises questions regarding the contamination of soils and groundwater and necessitates an evaluation of the relative risks and benefits¹². Infiltration ponds play a filtration and adsorption role to prevent the migration of pollutants¹³. Infiltration experiments have been conducted to estimate the fate of pollutants under laboratory conditions, using reconstituted soil columns and artificial runoff water¹⁴. Few studies were conducted under real conditions¹⁵ as presented here, but the results were promising: these studies showed a reduction in the environmental impact of roads without endangering road integrity, and an increase in aquifer recharge^{16,17}. The assays were conducted on a shortlist of pollutants, the most cited being metals, chlorides and PAHs^{13,18–20}. However, some laboratories also

worked on larger lists of suspected pollutants or performed research in a non-targeted manner, showing the presence of drugs and pesticides in runoff water or groundwater^{21,22}, these substances are usually not expected to be present in these matrices and are therefore not searched for.

Knowledge on how soil physico-chemical properties affect micropollutant trapping is scarce, and research is currently focussed on specific pollutant families^{23,24}. Therefore, the soil properties involved in micropollutant capture during ground infiltration are poorly understood. We measured micropollutant abundance in a road runoff treatment facility and monitored their distribution in sedimentation and infiltration ponds. We measured micropollutant abundance and soil physico-chemical properties at different depths in the infiltration pond from the surface to –165 cm. A chemical enrichment analysis indicated that a sedimentation pond is an indispensable part of every road runoff facility. A correlation analysis between micropollutant abundance and soil physico-chemical properties highlighted the involvement of sand abundance in the retention of micropollutants. Based on these results we propose a holistic model for soil physico-chemical properties affecting micropollutant accumulation in an infiltration pond.

RESULTS

Micropollutant distribution trend in a road runoff facility

The management of road runoff micropollutants is a complex task as a broad diversity of compounds with varied chemical properties must be addressed. The studied system is composed of a sedimentation pond from which water and sediment were analysed, and an infiltration pond from which soil was sampled at different depths (0–10, –80 and –165 cm) (map of the studied site is available in Supplementary Fig. 1). A road surface of 3.66 ha is drained to the sedimentation pond of the studied site. It receives 5400 vehicles per day, including ~400 delivery lorries. A total of 94 rain events (at least 1 mm of cumulated rain, the shorter rain events lasting 15 min) were recorded between July 2018 and July 2019, which brought a total of 410.8 mm of rain in 1

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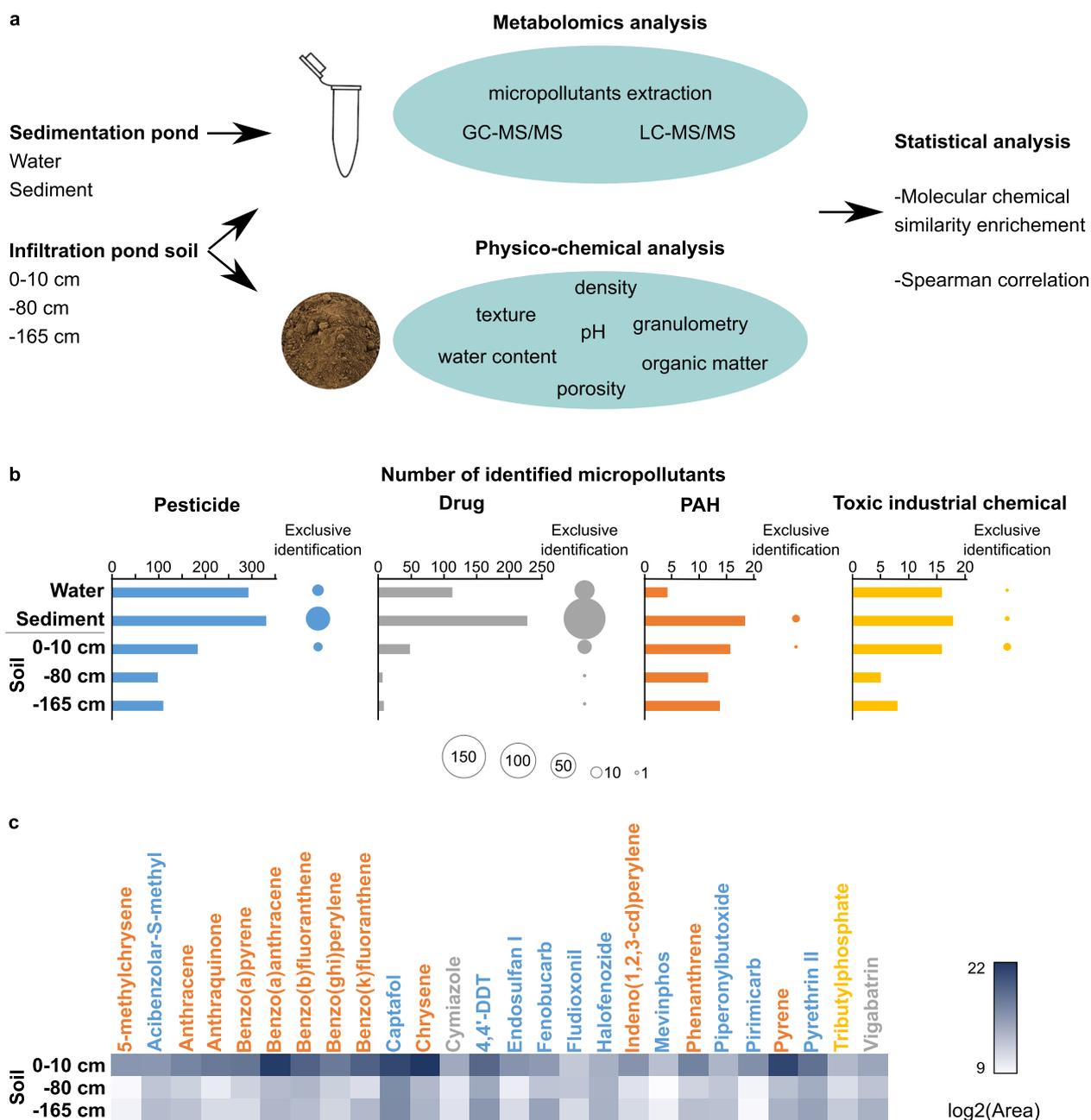


Fig. 1 Distribution of micropollutants in the water, sediment and soil layers. In a first attempt to describe the distribution of micropollutants in the sedimentation pond (water and sediment) and across the soil layers of the infiltration pond (from 0–10 to –165 cm in depth), micropollutants were categorized according to their most common usage: pesticide, drug, PAH and toxic industrial chemical were the prevailing categories identified. **a** Schematic representation of the study workflow. **b** Number of micropollutants identified in water, sediment and soil. Exclusive identifications indicate the micropollutants that were identified exclusively in one type of sample. **c** Distribution of micropollutants in the different layers of the infiltration pond soil presented as log₂ of the peak areas obtained from mass spectrometry analysis.

year (from 1 to 25 mm per rain event) (Supplementary Dataset 1). From water, sediment and soil samples, micropollutants were extracted and identified using mass spectrometry coupled with gas chromatography and liquid chromatography. Alongside these identifications, the physico-chemical properties of the soil from the infiltration pond were investigated. Statistical analyses were performed to investigate the distribution of micropollutants between water, sediments and soil using chemical enrichment, and the correlation between micropollutant abundance and soil physico-chemical properties (Fig. 1a). From the water, sediment and soil samples, micropollutants were identified and categorized

according to their most common usage. Pesticides, drugs, PAHs and toxic industrial chemicals were the most represented categories in terms of the number of micropollutants identified. Figure 1b shows the distribution of these categories among the different samples, as well as the exclusive presence of several micropollutants from a single sample type. These results show the importance of the sedimentation pond, as a higher number of pollutants from all categories were found in water and sediment. Additionally, the highest number of exclusive identifications is depicted in sediment from pesticides (48), drugs (142) and PAHs (4), highlighting the crucial role of this matrix trapping

micropollutants and avoiding their spread to the infiltration pond. In the infiltration pond, the soil surface (0–10 cm) retained a high number of micropollutants (184 pesticides, 48 drugs, 16 PAHs and 16 toxic industrial chemicals), reducing the number of compounds identified in the deeper layers of soil (Fig. 1b). A closer look at the abundance of the compounds confirms the role of the surface layer (0–10 cm), as the micropollutants that were detected in all the soil layers were found to be generally more abundant at the surface of the infiltration pond (Fig. 1c), with 39–99% of the micropollutants in terms of abundance, trapped in the surface layer (Supplementary Table 1). Mostly pesticides and PAHs could be found in all the layers of the infiltration pond soil. PAHs, metals and chlorides, which are common micropollutants encountered in road runoff water, were quantified in the samples (Supplementary Fig. 2). PAHs were confirmed to be more abundant in the surface layer of the infiltration pond than in the deeper layers, with 90–99% of the PAHs, in terms of abundance, trapped in the surface layer (Supplementary Table 1). Metals and chlorides were not further considered in this study because their concentration was under the French regulation thresholds²⁵.

Chemical enrichment analysis

To better describe the distribution of micropollutants in the studied matrices and to allow comparison with other studies, a chemical enrichment analysis was performed to obtain clusters of micropollutants based on structural similarity and chemical ontology (Fig. 2). A pair-wise statistical test was used to highlight increased (red) or decreased (blue) compounds, and clusters containing both increased and decreased compounds are depicted in purple. The size of the circles indicates the number of compounds in the cluster, and only significantly impacted clusters of a minimum of three compounds are shown on the graph. The position of the clusters on the x-axis depends on their partition coefficient, expressed as the median XlogP value (hydrophilic compounds on the left and hydrophobic compounds on the right).

The first comparison was made between sediment and water (Fig. 2a) to understand the behaviour of micropollutants in the sedimentation pond and their distribution among the liquid and solid matrices. The distribution of the clusters on the x-axis depicts a rather high variability in terms of hydrophobicity, ranging from very hydrophilic aniline compounds to very hydrophobic benzene derivatives and fluorenes (PAHs). Nevertheless, all the clusters are coloured red, which indicates that all the compound families are increased in the sediment samples compared to the water samples. Micropollutants trapped in sediment do not seem to be released to the infiltration pond, as demonstrated by the chemical enrichment analysis between the infiltration pond (all layers) and the sedimentation pond (water and sediment) (Fig. 2b). All but two clusters were decreased in the infiltration pond, and almost the same clusters appeared in this analysis compared to the sediment/water comparison. Organothiophosphorus compounds and isoindoles are depicted in purple, which means that only part of the compounds from this family was increased, while others were decreased (details are available in Supplementary Dataset 2). Chemical enrichment analysis revealed six clusters that were always found to be significantly impacted, regardless of the pairwise comparison made: aniline compounds, organothiophosphorus compounds, benzene derivatives, pyrethrin, benzopyrenes and fluorenes. The analysis also confirms the crucial role of the sedimentation pond in trapping micropollutants (in terms of not only in the number of micropollutants but also in abundance), which are mostly retained by sediment, regardless of their hydrophilicity, while logP (also known as log Kow) is often said to be one of the key indicators of micropollutant distribution in the environment²⁶.

Correlation of soil properties and micropollutant abundance

To understand the fate of micropollutants in the soil during infiltration, three clusters with distinct hydrophobicity were chosen (Fig. 2): aniline compounds (median XlogP < 2), pyrethrins (median XlogP ≈ 4) and benzopyrenes, which were grouped with fluorenes (median XlogP > 6), as these two clusters are described as PAHs in the literature even though the chemical ontology separates them. These three clusters were used to investigate the correlations between compound abundance and soil physico-chemical properties (Fig. 3). Correlation coefficients were interpreted as negligible to highly positive/negative as described in the literature²⁷.

The first piece of striking evidence is that the positive or negative trends were the same for all micropollutant families, regardless of the median XlogP value. A gradient was observed, with higher absolute values of the correlation coefficients for the compounds with lower median XlogP values. The abundance of aniline compounds was positively correlated with depth, percentage of coarse elements and sand, soil density and organic matter content, with a high correlation coefficient of 0.88 ($P < 0.01$) for all correlations. This indicates that the abundance of the compounds increased as these soil parameters increased. The abundance of aniline compounds was negatively correlated with water content and soil pH with a high correlation coefficient of -0.88 ($P < 0.01$), which indicates that the abundance of the compounds decreased when water content and pH increased. The presence of sand and clay seemed to help in PAH capture, as moderate positive correlations were observed (0.64 ($P < 0.001$) and 0.46 ($P < 0.05$) respectively) while the percentage of silt was highly negatively correlated with PAH abundance (-0.73 , $P < 0.001$). Pyrethrins showed the same trends as aniline compounds and PAHs, with correlation coefficients (absolute values) between those of the two other compound families.

The curvature coefficient obtained for the different soil layers was between 4.05 and 4.44; therefore, the soil in the infiltration pond was not well graded. The defined particle sizes were 1.26–1.38 μm (d10), 20.7–22.73 μm (d50) and 101.1–161.2 μm (d99) (Supplementary Table 2). The largest particles of the soil ($>100 \mu\text{m}$) were the best suited to retain micropollutants with a high positive correlation between micropollutant abundance and the d99 value (0.87, $P < 0.05$; 0.85, $P < 0.01$; 0.79, $P < 0.001$). Indeed, smaller particles showed a low negative correlation with pyrethrin and PAH abundance (-0.44 and -0.46 , respectively, $P < 0.05$) and the high to moderate positive correlations between micropollutant abundance and the percentage of coarse elements confirm this hypothesis (0.88, $P < 0.01$; 0.73, $P < 0.001$ and 0.64, $P < 0.001$). The water content (19–21%) and pH value (6.7–7.1) did not vary much between the layers of the soil and did not seem to help in micropollutant trapping in the surface layer of the infiltration pond. The abundance of micropollutants increased as the water content decreased (-0.8 , $P < 0.01$; -0.37 , $P < 0.001$; -0.64 , $P < 0.001$), but in an infiltration pond, it is not possible to reduce the amount of water since the primary function of the pond is infiltration. Regarding pH, the correlation coefficients were the same as those for water content, indicating that micropollutant abundance increased when pH decreased, which can be managed if necessary. Porosity was not correlated with the abundance of any of the compound families presented here.

The content of organic matter was high to moderately correlated with micropollutant abundance (0.88, $P < 0.01$; 0.73, $P < 0.001$, 0.64, $P < 0.001$). The organic matter was highest in the surface layer (6 mg/g) and decreased with depth (-80 cm , 5.2 mg/g; -165 cm , 4.7 mg/g). As the soil surface layer also harbours living organisms and plant root systems, the ratio of plant root systems and soil was investigated at four distinct sampling points situated 30 cm around the coring site (Table 1). The presence of small organisms and microorganisms could not be studied due to the lack of technical means.

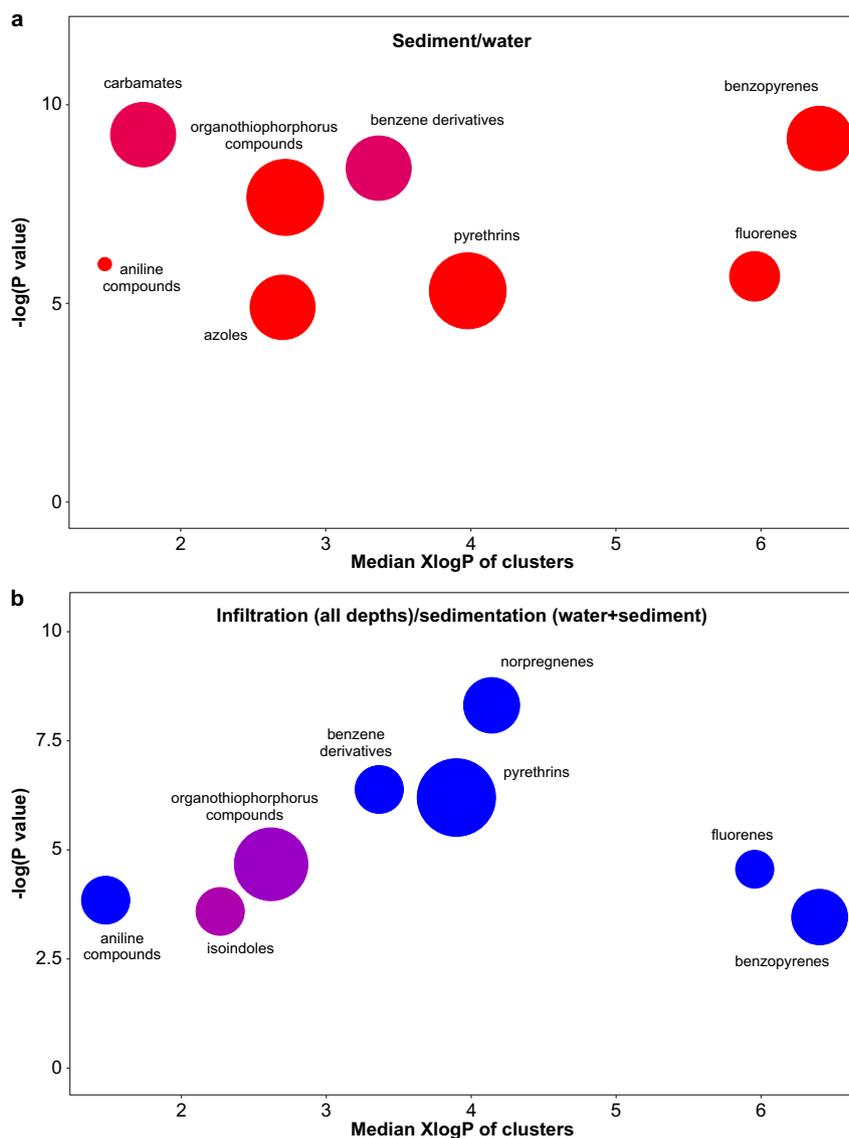


Fig. 2 Chemical enrichment analysis of sediment/water and infiltration/sedimentation samples. Significantly impacted metabolite clusters ($P < 0.05$) are depicted in red (increased) and blue (decreased). The most significantly altered clusters are shown on the top of the y-axis; clusters are distributed on the x-axis based on their partition coefficient (hydrophilic compounds on the left and hydrophobic compounds on the right). The size of the circles indicates the number of compounds in each cluster. **a** Chemical enrichment between sediment and water and **b** chemical enrichment analysis between infiltration (all depth) and sedimentation (water + sediment). Chemical enrichment statistics were calculated by the Kolmogorov–Smirnov test.

Roots in the top 10 cm of the infiltration pond represented between 10.9 and 35.5% of the total soil dry weight (Table 1), indicating that micropollutants identified in the surface layer of the infiltration pond might interact with not only mineral matter but also living organisms, including plant roots that can represent up to 1/3 of the soil dry weight. The plant diversity at the studied site was important, and many spontaneous plants settled at this location by themselves. The water content was comparable between roots and soil samples for each sampling area (Table 1), helping micropollutant exchange through the water flux between soil particles and plant roots.

DISCUSSION

The distribution of a complex mixture of road runoff micropollutants was investigated in a treatment facility composed of a sedimentation pond, followed by an infiltration pond. Of the 2406

micropollutants investigated, 700 were identified in the different matrices studied. The critical role of the sedimentation pond was demonstrated here, not only in terms of the number of micropollutants retained (610 in total, Fig. 1) but also with regard to the abundance of micropollutants (Fig. 2) with a mean trapping of 79% of the abundance of micropollutants, reaching 91–98% for PAHs (Supplementary Table 1). The identified micropollutants were distributed mainly in the sediment part of the pond, with only a few identified compounds specific to the water part (33 drugs, 11 pesticides and 1 toxic industrial chemical). One could have expected hydrophilic compounds to stay in solution in the water matrix and hydrophobic compounds to be sequestered by suspended solids and to settle and form sediment^{28,29}. However, this is a very favourable result, as it shows that micropollutants were trapped in the sedimentation pond and that release to the infiltration pond and to the environment was avoided. The presence of the sedimentation pond prevents the spread of

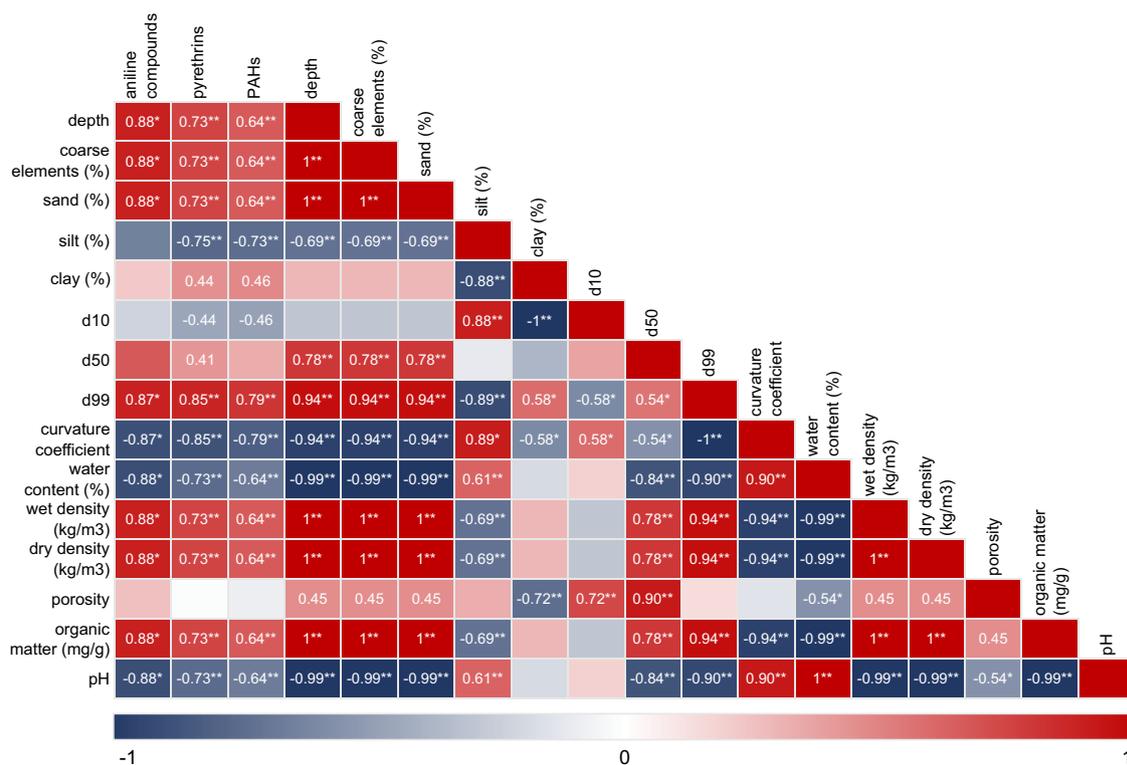


Fig. 3 Correlation matrix between the abundance of micropollutants of interest and the physico-chemical properties of the soil in the infiltration pond. Correlation coefficients were calculated using Spearman's correlation; positive coefficients (red) indicate a positive relationship between the variables, and negative coefficients (blue) indicate a negative relationship. Values near zero (white) indicate no relationship between the variables. Correlation coefficients are indicated only if $P < 0.05$; asterisks indicate $P < 0.01$ (*) and $P < 0.001$ (**). $N = 9$ (aniline compounds), 24 (pyrethrins), 27 (PAHs). d10, 1.26–1.38 μm particles; d50, 20.7–22.73 μm particles; d99, 101.1–161.2 μm particles.

Table 1. Determination of roots and soil proportions in soil samples.

	Sample 1		Sample 2		Sample 3		Sample 4	
	Roots	Soil	Roots	Soil	Roots	Soil	Roots	Soil
Wet weight (g)	28.6	37.95	43.71	48.06				
Dry weight (g)	20	29	35.9	37.8				
Wet weight (g)	12.3	16.3	8.45	29.5	3.90	39.81	7.9	40.16
Dry weight (g)	7.1	12.9	5.9	23.1	3.9	32	5.4	32.4
Water content (%)	7.5	7.5	2	1.7	1.9	1.9	2.1	2.1
% of total sample (dry weight)	35.5	64.5	20.3	79.7	10.9	89.1	14.3	85.7

Samples were collected from the top 10 cm of the soil, at 30 cm from the coring site in four directions. Roots and rhizomes were manually separated from the soil to estimate the root and soil content of the surface layer of the infiltration pond.

micropollutants, thereby protecting soil and groundwater from contamination, as previously described in the literature^{30–32}.

Moreover, the surface layer of the infiltration pond showed high efficiency in retaining micropollutants from infiltrating into the deeper layers of the soil. The observation that road runoff pollutants are sequestered in the surface layers of soils has already been made in the previous studies^{13,33,34}. The number of micropollutants trapped in the surface layer is important (269 micropollutants, Fig. 1b), and the abundance of micropollutants detected in the surface layer is much more important than in the other layers, with a mean value of 86% of the abundance of micropollutants trapped at the surface (Supplementary Table 1,

Fig. 1c and Supplementary Fig. 2). The correlation analysis with soil properties provides some clues regarding how to maintain and increase the natural abilities of the infiltration soil to retain micropollutants.

A previous study that focussed on per- and polyfluoroalkyl substances already showed that multiple soil properties are involved in pollutant retention²³. Other studies also present interesting results regarding soil physico-chemical parameters as pH or organic matter content affecting the soil–solution partitioning of metals^{26,35,36}. Here, a correlation analysis was performed using three chemical families of micropollutants with varied median XlogP values, to identify general observations suitable for most of the micropollutants encountered in road runoff facilities. The positive and negative correlation trends were the same for all the considered families, and a gradient was observed in the correlation coefficients, with higher coefficients (absolute value) for compounds with lower median XlogP values. The proposed results are applicable to pollutants with median XlogP values ranging from <2 to >6 , as presented in this study. Five soil properties were identified as being negatively correlated with micropollutant abundance, while seven properties were identified as being positively correlated (Fig. 4a). The analysis shows that a higher proportion of sand with a large particle size was better suited for the retention of micropollutants with different median XlogP values in the surface layer of the infiltration pond. The presence of clay might aid the trapping of micropollutants with higher median XlogP values. Silt and particles with a size $<20 \mu\text{m}$ should be avoided. The studied soil properties are known to affect soil permeability, which might impact the retention time and therefore the adsorption capacity of the infiltration pond soil towards micropollutants. The soil pH value was negatively correlated with micropollutant abundance; therefore, decreasing the pH of the infiltration pond soil could be

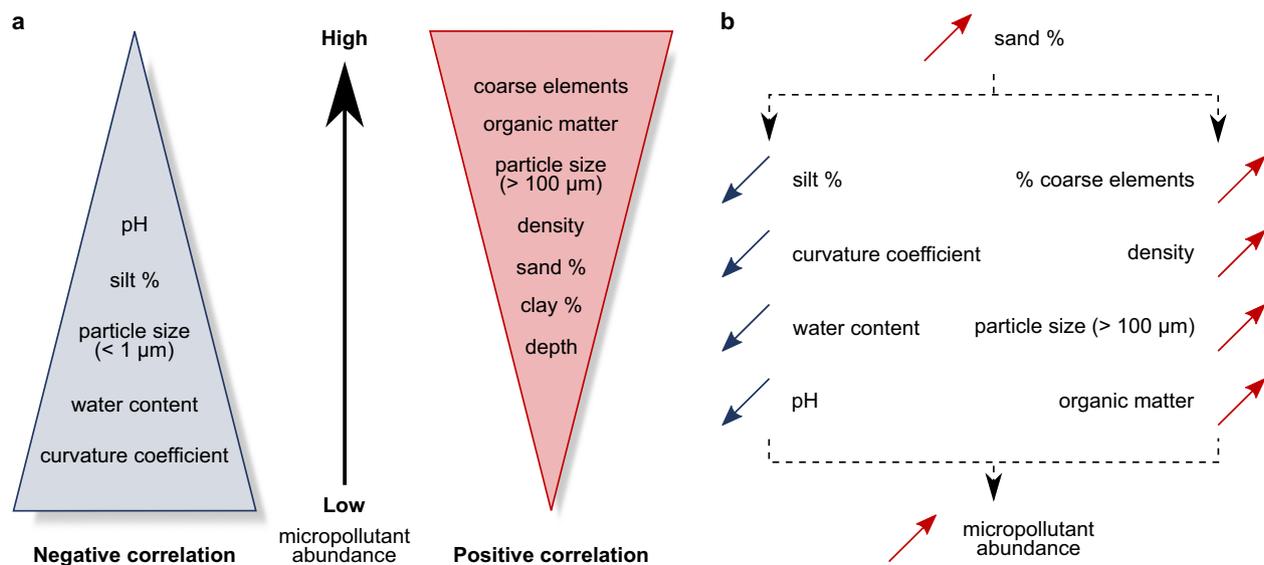


Fig. 4 Proposed model for soil physico-chemical parameters affecting micropollutant abundance in a road runoff infiltration pond. a Soil properties could be divided into those that are negatively (blue) and positively (red) correlated with micropollutant abundance. **b** A strategy is proposed to increase micropollutant trapping in the soil of an infiltration pond.

a suitable management practice for use in infiltration ponds. The correlation between pH and the proportion of sand was very highly negative (-0.99 , $P < 0.001$), indicating that increasing the proportion of sand would lower the pH, and therefore help in micropollutant trapping as the micropollutant abundance increases with increasing amounts of sand and decreasing pH. The organic matter content was very highly correlated with the proportion of sand in the pond. Once again, increasing the proportion of sand would increase the organic matter content and help in micropollutant retentions. Moreover, better retention of PAHs in soil fractions containing organic matter has been previously reported³⁷. A management strategy is proposed, wherein the central element is the proportion of sand in the soil (Fig. 4b). Sand is mainly composed of silica, which is used in chromatography to adsorb molecules according to their polarity. Therefore, we hypothesize that sand particles with a large size ($>100 \mu\text{m}$) offer a large contact surface and might be well suited to help the adsorption of micropollutants, to trap them and avoid infiltration to the deeper layers of the soil. A moderate efficiency of sand in the removal of micropollutants has already been described³⁸. In addition to this adsorption capacity, sand is a good host for bacteria, which form a biofilm able to accumulate micropollutants. It has been demonstrated that the presence of a biofilm in a sand filter increases its micropollutant removal efficiency³⁹. Therefore, the role of sand in micropollutant removal would be due in part to adsorption, but also to accumulation in the biofilm.

One should also keep in mind that biodiversity in soils is known to have a role in micropollutant trapping and biodegradation. The Food and Agriculture Organization stated that “One teaspoon of soil contains more living organisms than there are people in the world”⁴⁰. One gram of soil can contain up to 1 billion bacterial cells, 200 m of fungal hyphae and several thousand different taxa of macroorganisms, and the total biomass below ground would equal or potentially exceed that above ground⁴⁰. Therefore, the role of soil microorganisms in trapping and transforming micropollutants should be considered. These organisms range from 20 nm to 20–3 cm in body size and can be divided into four size classes: microbes (20 nm–10 μm), mesofauna (0.1–2 mm), macrofauna (2–20 mm) and megafauna ($>20 \text{mm}$)⁴⁰. Soil microorganisms participate in soil structure, decomposition of organic matter, water retention, soil aeration and movement of soil

particles through different layers. For example, bacteria have already been described to be the most active in the top 10 cm of soil in the context of constructed wetlands⁴¹. The size of soil particles and the size of organisms are closely related: larger organisms (from vertebrates to nematodes) are found in sandy soils; fungi, protozoa and some algae are found in silt; and other bacteria, archaea and viruses are found in clay⁴². Plants can establish their roots in sandy to silty soils and interact closely with soil organisms. They perform phytoextraction in their aerial parts and phytostabilization in their underground root system through absorption and accumulation, adsorption onto roots or precipitation within the root zone, which decreases the bioavailability of micropollutants in the soil and reduces ecotoxicity⁴³. Plant diversity is a key player in micropollutant management, as each plant manages a distinct pool of micropollutants, with some of them being specific to certain plants⁴⁴. Spontaneous plants are well suited for micropollutant management, as they naturally adapt to the constraints of the environment, settle only if they can survive in the presence of micropollutants and do not need any care. Preserving the natural biodiversity in facilities is also a way to avoid the spread of micropollutants.

From the results obtained in this study, a model is proposed for soil physico-chemical parameters that affect micropollutant abundance in a road runoff infiltration pond, regardless of their median XlogP value. These results are applicable for micropollutants under real conditions in a road runoff treatment facility composed of a sedimentation pond and an infiltration pond. The curvature coefficient, water content, small soil particles ($<1 \mu\text{m}$), silt proportion and pH are soil physico-chemical parameters that are negatively correlated with micropollutant abundance. This means that these parameters decrease when the abundance of micropollutants increases. The presence of coarse elements, organic matter, large soil particles ($>100 \mu\text{m}$), density and the proportions of sand and clay are positively correlated with micropollutant abundance, which means that these parameters increase when micropollutant abundance increases.

To help in micropollutant trapping in an infiltration pond and avoid leaching to groundwater, a simple solution seems to be to increase the proportion of sand in the infiltration soil. Indeed, the proportion of sand is positively correlated with the presence of coarse elements and large particles (d₉₉), density and organic matter content, properties that are positively correlated with

micropollutant abundance. Moreover, the proportion of sand is negatively correlated with the proportion of silt, water content, curvature coefficient and pH, which are negatively correlated with micropollutant abundance. Therefore, increasing the proportion of sand would decrease negatively correlated parameters and help in micropollutant trapping. In addition to allowing and preserving the settlement of the natural biodiversity in the facilities, increasing the amount of sand in the infiltration pond is an easy solution that seems to interact well with all the studied soil physico-chemical parameters according to the correlation analysis. This solution is inexpensive and demands reduced primary inputs; moreover, the presence of small-scale vegetated sedimentation and infiltration ponds along roads is socially desirable and helps manage road runoff pollution at its source to prevent environmental contamination.

METHODS

Study site and sampling

The study site is situated in Wolfisheim, Alsace (France), along department road RD45 (48°35'38.353"N, 7°39'19.652"E) and was established in 2013. It is composed of a sedimentation pond collecting road runoff from 3.66 ha of road, followed by an infiltration pond to release water to the environment (a detailed view of the study site is provided in Supplementary Fig. 1). The sedimentation pond is lined and made of concrete to avoid the infiltration of runoff water at this step. Suspended solids from runoff water, which settled on the concrete floor of the sedimentation pond, were collected and referred to as "sediment" in all the manuscripts. Water and sediment were sampled from the entrance of the sedimentation pond. Soil from the infiltration pond and from the bank (used as a control) was sampled at the surface (0–10 cm), at –80 cm and at –165 cm using a manual auger. Three samples of each matrix were collected as replicates (individual samples that are considered representative of the studied matrix). All samples were stored in glass bottles and immediately placed at 4 °C in the dark for transport. Upon arrival at the laboratory, weighing of the sediment/soil and filtering of the water using a coffee filter were performed in a cold room (4 °C). Pollutants were extracted from fresh sediment and soil samples in the dark and without drying (see 'Correlation of soil properties and micropollutant abundance'). A weather station (Adcon Telemetry) was implemented on the site to record rain events every 15 min (Supplementary Dataset 1).

Four samples of surface soil (0–10 cm) were collected at 30 cm from the drilling point in four opposite directions to analyse the proportion of roots and soil in the samples. Roots were manually sorted from soil particles using surgical pliers. Samples were dried in an oven at 105 °C for 4 h before weighing the dry weight.

Chemicals

Solvents (acetonitrile, methanol and isopropanol) were purchased from Fisher Chemicals (New Hampshire, USA). Acetic and formic acids were purchased from Sigma-Aldrich (Missouri, USA), ammonium formate was purchased from Fluka Analytical (Missouri, USA) and NaOH was purchased from Agilent Technologies (California, USA). Deionized water was obtained from a Direct-Q UV station (Millipore, Massachusetts, USA). Pure standards of PAHs used for quantification were purchased as a mix from Restek (Lisses, France), ref. 31455. Analytical performance quality checks were performed with a mix of pesticides obtained from Restek (ref. 32563 for gas chromatography and refs. 31972 and 31978 for liquid chromatography).

Soil physico-chemical property measurements

All the soil layers were wet sieved at 2 mm and stored wet at 4 °C before soil characterization. Physico-chemical parameters were measured following standard analytical procedures (NF/ISO) on homogenized sediment samples, dried at 105 °C and sieved to 2 mm. Soil water content was measured by the mass difference after drying to constant mass (ISO 11465). The particle size distribution was measured by laser diffraction methods in water mode (LS230, Beckmann Coulter; ISO 13320). The results from the distribution were used to cluster the soil using three texture class levels following the World Reference Base⁴⁵ of soil: clay <2 µm, silt from 2 to 50 µm and sand from 50 to 2000 µm. Then, solid-liquid extraction was

used to remove the following phases: (1) organic matter was extracted by a 1:3 (v/v) solution of H₂O₂ at 60 °C, (2) cationic flocculants were extracted using KCl (1:50 (v/v)) or HCl (1:20 (v/v)) depending on the carbonate content of the sample and (3) desegregation of particles was performed by adding a 1:1 (v/v) solution of sodium hexametaphosphate 0.55%. Bulk density and porosity were obtained by following the French standard NF P94-410-3. The porosity measurement was performed using a water pycnometer. Organic matter content was determined by measuring the weight loss at 550 °C for 24 h (in-house method). The pH value was measured by following the standard NF EN 15933.

Metal and chloride analysis

The samples were analysed by EUROFINs (Saverne, France) for the quantification of aluminium, cadmium, copper, nickel, lead and mercury. Mercury was quantified using cold vapour atomic fluorescence spectroscopy following the French standard NF EN 13346-NF ISO 16772. Other metals were quantified using inductively coupled plasma-atomic emission spectroscopy following the French standard NF EN ISO 11885-NF EN 13346. Chlorides were quantified using potentiometry following the French standard NF EN ISO 10304.

Micropollutant extraction

The extraction methods for micropollutants from water and soil were developed in the laboratory using internal standards in representative samples, as already published by Villette et al.⁴⁶ Briefly, pollutants were extracted from 10 g of soil by performing a double extraction. The first overnight extraction was performed using 40 mL of acetonitrile:H₂O (90:10) and 1% acetic acid at 4 °C under shaking with a magnetic stirrer. The samples were centrifuged for 15 min at 5827 × g to collect the supernatant. A second extraction was applied to the pellet using 20 mL of isopropanol:acetonitrile (90:10) for 15 min at 4 °C under shaking. After a second centrifugation, the supernatants were pooled and freeze-dried. Samples were solubilized in 1 mL of acetonitrile:isopropanol:H₂O (50:45:5) and diluted 10 times in H₂O for liquid chromatography-high-resolution mass spectrometry (LC-HRMS) analysis or solubilized in 1 mL of ethyl acetate and diluted 2 times for gas chromatography-tandem mass spectrometry (GC-MS/MS) analysis.

Fifty millilitres of groundwater samples were freeze-dried under vacuum and recovered in 1 mL of MeOH:H₂O (90:10) and diluted 10 times in water for LC-HRMS analysis or recovered in 1 mL ethyl acetate and diluted 2 times for GC-MS/MS analysis.

LC-quadrupole-time-of flight-HRMS analysis

Samples were analysed by LC coupled with HRMS using a DioneX Ultimate 3000 (Thermo, Massachusetts, USA) coupled to a Q-TOF Impact II (Bruker, Bremen, Germany) using the TargetScreener method (Bruker), which allows targeted identification of micropollutants using a database containing 2072 pollutants (848 pesticides and 1224 toxicants), their retention time, their exact mass and the exact mass of their fragments in broad-band collision-induced dissociation (bbCID) fragmentation mode. Samples were analysed on a C18 column (AcclaimTM RSLC 120 C18, 2.2 µm, 120 Å, 2.1 × 100 mm², Dionex bonded silica products) equipped with an Acquity UPLC[®] BEH C18 pre-column (1.7 µm, 2.1 × 5 mm²) using a gradient of solvent A (H₂O:MeOH 90:10, 0.01% formic acid, 314 mg L⁻¹ ammonium formate) and solvent B (MeOH, 0.01% formic acid, 314 mg L⁻¹ ammonium formate) as described in detail by Villette et al.⁴⁶. The spectrometer was operated in positive ion mode using bbCID fragmentation mode in a mass range from 30 to 1000 Da, with a spectra rate of 2 Hz. Analytical quality checks were performed using a mix of pesticides to assess the retention times (refs. 31972 and 31978, Restek).

GC-MS/MS analysis

GC-MS/MS analysis was performed using GC coupled to a triple quadrupole detector (SCION 436-MS, Bruker). Samples were carried through a Rxi[®]-5Sil MS column (Restek, 30 m, 0.25 mm ID, 0.25 µm) with a constant flow (1 mL min⁻¹) of helium gas (Alphagaz 2, Air Liquide). The injector was operated at 280 °C with a pressure pulse at 30 psi, the oven was set at 70 °C for 0.7 min and the temperature was increased to 180 °C at 30 °C/min, and then to 300 °C at 10 °C/min, with a stabilization time of 2 min. The spectrometer was operated in multiple reaction monitoring (MRM) scan type with an electron energy of 70 eV to search for 328 micropollutants (pesticides, PAHs and toxicants). At least two daughter

ions were recorded for each analyte, and a retention window of 5 min was used. For quantification, a mix of PAH analytical standards (EPA 610 B, ref. 31455, Restek) was used and injected using the same method, and then standard curves were established manually. Analytical quality checks were performed using a mix of pesticides to assess the retention times (ref 32563, Restek).

MS data analysis

Micropollutants were identified to level 1 of the Schymanski classification⁴⁷ based on their retention time, exact mass of the parent ion and fragment ions when available using LC and GC. For LC-HRMS data analysis, the signal-to-noise ratio was set to 3, the retention time window was set to 0.25 min and the exact mass variation was set to 3 p.p.m. in the TASQ software (Bruker). A list of 2072 micropollutants was investigated, and the identification was confirmed based on the retention time, exact mass, isotopic pattern of the parent ion and at least one daughter ion obtained from the bbCID collision mode used on the spectrometer; identification was performed via interrogation of pesticide and toxic chemical databases. For GC-MS/MS data analysis, the signal-to-noise ratio was set to 3, the retention time window was set to 0.25 min and the mass variation was set to 0.5 Da in MS Data Review software 8.2 (Bruker). The presence of at least two daughter ions obtained from the MRM mode on the spectrometer confirmed the identification results from the list of 328 micropollutants investigated.

Labelled internal standards were used to assess the repeatability of the extraction process and to determine the limits of detection and quantification⁴⁶, and the coefficients of variation obtained were in accordance with already published literature⁴⁸.

Statistical analysis

Statistical analyses of the whole dataset were performed using the area of the peaks as the unit of reference. The dataset obtained from LC-HRMS and GC-MS/MS experiments (see Section 2.7) and containing the names of the compounds and the areas of the peaks in the different soil layers was imported into Metaboscape 4.0 (Bruker) as a csv file for statistical analysis. The thresholds used to indicate a significant difference were $P \leq 0.05$ and fold change ≥ 2 or ≤ -2 . Due to the small number of samples (three replicates for each condition), the nonparametric Wilcoxon's rank-sum test was used.

Chemical enrichment analysis was performed on the pollutants identified using the online version of the ChemRICH tool⁴⁹. To generate the dataset for ChemRICH interrogation, chemical identifiers (PubChem ID, InChIKey and SMILE) were manually recovered from the names of the compounds using the PubChem Identifier Exchange Service (<https://pubchem.ncbi.nlm.nih.gov/idxchange/idxchange.cgi>). These identifiers are necessary for the tool to estimate the structural similarity between the compounds based on chemical ontologies. The statistical information was then used to propose a statistical enrichment approach and highlight the compounds that were up- or downregulated under a specific condition. The whole dataset (significantly differential and non-differential values) was submitted to ChemRICH, with the fold change converted to the average ratio. The ChemRICH thresholds were $P \leq 0.05$ and fold change ≥ 2 or ≤ -2 to indicate whether a compound was significantly up- or downregulated under a specific condition and to obtain the chemical enrichment analysis results.

The correlation coefficients between micropollutant abundance and soil physico-chemical properties were calculated using Spearman's correlation due to the small number of observations and the presence of continuous and ordinal variables²⁷. The correlation matrix was created from the obtained coefficients and is presented with a gradient of blue (negative correlation) to red (positive correlation). The coefficients are indicated in the matrix only if $P < 0.05$ for the corresponding correlation. Correlation coefficients were considered very high (0.9–1.0) to negligible (0.0–0.3) according to a previously proposed ref.²⁷

For quantification data, statistical analysis was performed in R3.6.1 to search for significant differences in metal, chloride and PAH concentrations between the bank and the pond.

DATA AVAILABILITY

The datasets generated and analysed during the current study are available from the corresponding author on reasonable request.

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AUTHOR CONTRIBUTIONS

L.M. sampled the soil, prepared the samples, analysed the data, prepared the figures and discussed the manuscript. C.V. designed the experiment, injected the samples for LC-HRMS, analysed the data, prepared the figures and wrote the manuscript. J.Z. injected the samples for GC-MS/MS and discussed the results. C.L. and M.P.O. performed the metals and chlorides analysis. A.W. discussed the results and manuscript. D.H. designed the experiment, discussed the results and the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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