frontiers | Frontiers in Environmental Science

TYPE Original Research
PUBLISHED 03 April 2023
DOI 10.3389/fenvs.2023.1125487

OPEN ACCESS

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SPECIALTY SECTION
This article was submitted to Soil Processes,
a section of the journal
Frontiers in Environmental Science

RECEIVED 16 December 2022
ACCEPTED 20 March 2023
PUBLISHED 03 April 2023

CITATION
Maurin N, Sayen S and Guillon E (2023), Gas chromatography–mass spectrometry analysis of organic pollutants in French soils irrigated with agro-industrial wastewater.
Front. Environ. Sci. 11:1125487.
doi: 10.3389/fenvs.2023.1125487

Gas chromatography–mass spectrometry analysis of organic pollutants in French soils irrigated with agro-industrial wastewater

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The use of agro-industrial wastewater in the agricultural sector is an interesting practice to save resources but it can bring various contaminants to the receiving soils. In this study 19 organic pollutants [8 polycyclic aromatic hydrocarbons (PAH), 6 BTEX, 4-tert-octylphenol, 4-octylphenol, 4-n-nonylphenol, tributyltin and diethylphtalate] were analyzed by gas chromatography-mass spectrometry (GC-MS) in soils irrigated with agro-industrial wastewater from sugar refinery. The soils were sampled at five different locations to evaluate the contamination heterogeneity. Microwave-assisted extraction (MAE) was performed using methanol and hexane and extraction yields ranged from 44% to 96%. The detection limits of the method were between 1.6 and 64 $\mu g \cdot L^{-1}$ for polycyclic aromatic hydrocarbons, 0.42 $\mu g \cdot L^{-1}$ for diethylphthalate, 0.77 $\mu g \cdot L^{-1}$ for tributyltin and until 9.8 $\mu g \cdot L^{-1}$ for phenol compounds. The highest contaminant concentrations measured in the soil samples, between 0.4 and 1.2 $ng \cdot g^{-1}$, were monitored for polycyclic aromatic hydrocarbons molecules, including napthalene, anthracene, fluoranthene, indeno(1,2,3-c,d)pyrene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[ghi]perylene. Toluene, ethylbenzene, xylene isomers accounted from 21 to 66 $ng \cdot g^{-1}$ (mostly toluene). Benzene, 4-tert-octylphenol, 4-octylphenol, 4-n-nonylphenol, tributyltin and diethylphtalate were not detected in soils. The proposed method enables analysis of a wide variety of regulated compounds in a unique preparation step and a unique analytical method. The mean amounts of pollutants were in agreement with measurements or estimates performed in similar contexts.

KEYWORDS

agro-industrial wastewater, soil, gas chromatography, mass spectrometry, organic contaminations, field measurement

1 Introduction

The increasing world population and associated resource consumption make water reuse a significant concern. Human activity uses about 4,600 km^3 of water yearly and a 20% increase is projected for 2050 (Burek et al., 2016). Irrigation, industrial and municipal uses account for 70%, 19%, and 11%, respectively. Hence water reuse, as a water source, represents a mean to reduce wastewater footprint as well as plant nutrients for agriculture. In addition, as wastewater contain nitrogen, phosphorus, potassium and organic carbon, it serves as plant nutrients for agriculture. As these nutrients usually need energy to be produced, recycling water is also a source of energy saving. That's why wastewater from municipal treatment plant or agro-industrial plant as an agricultural resource is used in several countries (Brockmann et al., 2018).

However, due to its previous uses in various activities, wastewater can be loaded with undesired products such as hazardous chemical substances towards human or crop growth. The stability and chemical properties of these organic pollutants result in their accumulation in the topsoil due to its rich organic content (Holoubek et al., 2009). Consequently, many countries have put in place regulations to limit the emission of pollutants in wastewater in order to preserve its quality for reuse. In Table 1 is shown the list of dangerous substances in the environment and the corresponding quantification limits needed to monitor water quality in France in 2014 (Ministère de l'écologie du développement durable et de l'énergie, 2014). It includes five classes of molecules such as polycyclic aromatic hydrocarbons (PAH), alkylphenols, phthalates, organotin and benzene, toluene, ethylbenzene and xylenes (BTEX). Fees are applied on non-domestic wastewater based on pollutant concentrations. Hence, monitoring the output of these substances has become an economical concern for agro-industrial actors reusing wastewater.

In France, contaminants in soils are monitored by the French National Soil Monitoring Network (Réseau de Mesures de la Qualité des Soils—RMQS). Several studies focused on the persistence in soils of PAHs by assessing the impact of atmospheric flux and road transportation (Clément et al., 2015; Gaspéri et al., 2018). BTEX are emitted by vehicle combustion in the atmosphere and then carried by rain into soils by leaching the atmosphere (Popescu and Popescu, 2017). Alkylphenol ethoxylates are found in several goods such as detergents, pesticides, inks, and paper leading to octylphenol and nonylphenol by degradation. They have been detected at high concentrations in soils and few countries have legislation about their concentration in agricultural soils (Llorca-Pórcel et al., 2009; Pérez et al., 2012). Tributyltin is known to be toxic for numerous organisms including humans. Many of industrial or domestic products like fungicides, insecticides, bactericides, wood preservatives and polyvinyl chloride (PVC) stabilizers have been recognized as potential sources of contamination (Champ, 2000). Phthalates have numerous applications such as automotive manufacturing and packaging. Diethylhexyl phthalate may reach up to 50% in PVC composition, and as it is not chemically bound to the polymer, it can be easily released in the environment during PVC production as well as end-product use, storage, or degradation (Heudorf et al., 2007). For these compounds, sludge application is one of the most important sources of agricultural soil contamination (Marcic et al., 2006). Thereby, monitoring the concentration of these pollutants is important to maintain the quality of agricultural soils.

All these contaminants were previously analyzed in soils by mass spectrometry using several extraction methods. PAHs were classically analyzed by gas chromatography coupled with mass spectrometry (GC-MS) (Poster et al., 2006). Their soil extraction was performed using various techniques such as soxhlet extraction, microwave assisted extraction (Wang et al., 2007; Xu and Lee, 2008) and pressurized liquid extraction (Gibson et al., 2005; Martínez Vidal et al., 2009). Alkylphenols can also be analyzed using GC-MS (Gibsons et al., 2005) after soil extraction with pressurized liquid extraction (Andreu et al., 2007) or microwave assisted extraction (Pérez et al., 2012). Heroult et al. (2008) compared several extraction techniques for tributyltin analysis in soils including mechanical stirring, accelerated solvent, microwave and ultrasonic extraction also using GC-MS. Phthalates analysis in soils was performed by liquid or gas chromatography after ultrasonic extraction (Ma et al., 2005) or microwave extraction (Chee et al., 1996; Liang et al., 2010). From these different studies, microwave extraction followed by GC-MS analysis was found to be a reliable analytical method for the monitoring of these pollutants. As for the BTEX class compounds, they are usually extracted from soils *via* headspace chromatography (Ezquerro et al., 2004; Shin, 2012) or liquid-liquid extraction (Khajeh et al., 2014) and to our knowledge no extraction was performed using a microwave oven. Thus it is important to optimize the methods allowing to analyze the whole set of compounds of concern which have various properties in a simple and fast way while respecting the performances required by the legislator.

In this context, this study aims at standardizing the extraction and analysis (quantification) of these different compound families with low detection limits. For this purpose, five soils sampled in different sites irrigated with wastewater from agro-industrial plant were analyzed by GC-MS using microwave-assisted extraction (MAE) targeting the organic substances identified by the French regulation.

2 Materials and methods

2.1 Sample sites

Five sites were sampled to characterize their physico-chemical properties in the Grand Reims area (Figure 1), which is an intercommunal structure located in the Grand Est Region (France) with 300,699 inhabitants in 2019 and a population density of 211/km^2. Agriculture in this area fall into four main activities which are vineyard, beets and alfalfa. Beet cultures are valorized locally in several products such as sugar, ethanol and alcohol. The area of the sampling site is a large beet agricultural zone crossed by active traffic roads, close to the Reims airfield, agricultural facilities and concrete industry. Several villages with a population between 500 and 1,000 inhabitants are surrounding the sites in a 2 km radius in addition to the city of Reims located 5 km west. All these activities may act as indirect sources of pollutants especially combustion residues. The cultures were spread with the effluents of a sugar factory at a 600 m^3·ha^{-1} (60 mm) maximum rate with a minimum of 2 years between each spreading on the same parcel. Land application with such effluents started in 1978. Only the data focusing on the nutritious capacity of the effluents were available. The concentrations of targeted pollutants were not known. Soil samples were provided by the association of agronomic spreading monitoring (ASAE, France). The sampling was focused on the rich organic content layer of the soil where the pollutants can accumulate. The topsoil was collected with a shovel until 25 cm depth and stored in a closed polyethylene bag at 4°C before use. The soils were characterized for particle size distribution without decarbonation, pH, cation exchange capacity (CEC), organic carbon (OC), and $CaCO_3$ contents according to French and International standard methods, following NF X31-107, ISO

TABLE 1 Quantification limits, detection limit, linearity and extraction yield of the method.

Analytes	Quantification limit (LOQ) required by the regulator (ng·g^{-1})	Quantification limit (LOD) (µg·L^{-1})	Quantification limit in soil (LOQ) (ng·g^{-1})	Detection limit in soil (LOD) (ng·g^{-1})	Linearity r^2	Extraction yield ± standard deviation (%)
Benzo(k)fluoranthene	10	3.4	0.37	0.1	0.9999	52 ± 2
Benzo(b)fluoranthene	10	2.4	0.27	0.1	0.9999	50 ± 4
Benzo(a)pyrene	10	1.6	0.18	0.1	0.9999	49 ± 8
Indéno(1,2,3-c,d)pyrene	10	3.6	0.40	0.1	0.9999	49 ± 7
Benzo(g,h,i)perylene	10	3.2	0.35	0.1	0.9999	54 ± 3
Anthracene	10	1.9	0.22	0.1	0.9999	57.3 ± 0.7
Fluoranthene	10	4.6	0.50	0.2	0.9999	62.7 ± 0.8
Naphtalene	10	64	5.0	1.5	0.9997	68 ± 2
Benzene	10	0.3	0.2	0.1	0.9997	79 ± 7
Toluene	50	0.5	0.5	0.1	0.9916	96 ± 2
Ethylbenzene	10	1.6	0.7	0.2	0.9999	81 ± 5
Xylene (o)	10	0.9	0.2	0.1	0.9999	83 ± 6
Xylene (m + p)	10	1.4	0.6	0.2	0.9999	72 ± 2
Diethylphtalate	25	0.42	3.1	0.9	0.9999	90 ± 10
Tributyltin cation	10	0.77	2.5	0.7	0.8797	40 ± 10
∑ Octylphenols	100	—	—		—	—
∑ Nonylphenols	100	—	—		—	—
4-Octylphenol	100	6.7	47.2	14.2	0.9929	90 ± 10
4-tert-octylphenol	100	9,8	68.9	20.7	0.8700	63 ± 8
4-n-nonylphenol	100	7.7	55.5	16.6	0.9762	91 ± 3
∑ 4-nonylphenol	100	—	—		—	—

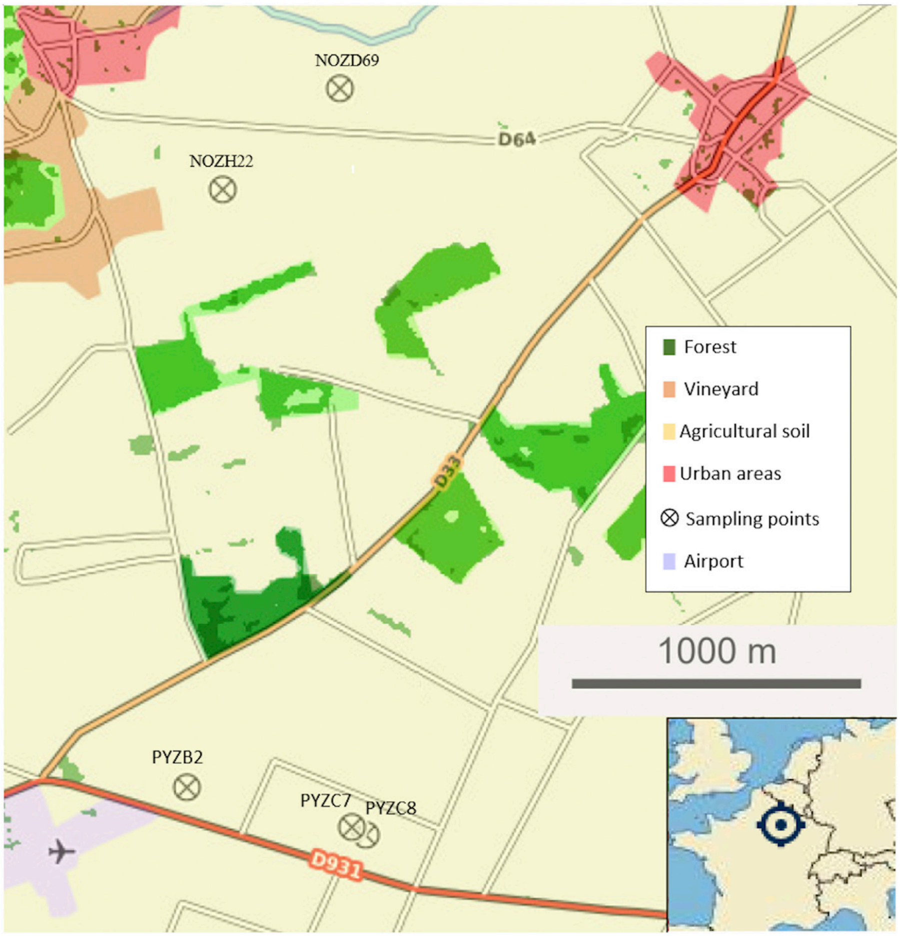

FIGURE 1
Sample locations: the five soil samples are represented by a circled cross (© IGN 2022).

10390, NF X 31-130, ISO 14235, and ISO 10693, respectively (AFNOR, 1995; AFNOR, 1998; AFNOR, 1999; AFNOR, 2003; AFNOR, 2005). Organic matter (OM) content was calculated as follows: % OM = 1.72% OC.

2.2 Chemicals and reagents

Methanol and hexane (HiPerSolv Chromanorm), as well as nylon filter (0.2 µm) syringes and filter supports were purchased from VWR. The standards benzo(k)fluoranthene, benzo(b) fluoranthene, benzo(a)pyrene, indéno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, anthracene, fluoranthene, naphtalene, benzene, toluene, ethylbenzene, xylene (o,m,p), diethylphtalate, tributyltin, 4-octylphenol, 4-tert-octylphenol, 4-n-nonylphenol were of the highest purity and purchased from Sigma Aldrich.

2.3 Microwave assisted extraction

Soil extraction was performed using a Thermo Scientific Ethos Easy microwave extractor with a Fast-24 rotor. The samples in glass tubes were subjected to a 1,800 W power to reach 110°C in 10 min, this temperature was then maintained during 10 min. PAH and BTEX compounds were extracted from 2 g of soils in 10 mL of hexane; for diethylphtalate, tributyltin and phenolic compounds, 5 g of soils in 10 mL of methanol were used. After microwave extraction the liquid phase was filtered through a nylon membrane and stored in a glass tube. The solvent was then evaporated to dryness in a centrifugal concentrator Genevac HT Series (SP Scientific, Warminster, PA, United States). The manufacturer programs "very low boiling point" and "medium boiling point" were used for hexane and methanol extraction respectively. The temperature was set at 40°C with a rotation speed of 1,400 rpm. The evaporation process started with a decrease in pressure from the atmospheric pressure to full vacuum in 1 h and was maintained for 6 h. The residue was dissolved in 500 µL of methanol and put inside a micro-vial for GC-MS analysis.

2.4 GC-MS analysis

The target compound concentrations were determined using a Thermo Scientific TRACE 1300 GC system coupled to a Thermo

Scientific ISQ Series quadrupole mass spectrometer equipped with an electronic impact source (Low activity). The separation was achieved by injecting 0.5 µL of the sample in a Thermo Scientific TR5-5MS column (30 m, I.D. 0.25 mm, film 0.25 µm). Data were processed with the XCalibur™ 2.2 software. Injection was made in splitless mode. The transfer temperature was set at 250°C with a source at 230°C. The dwell time was set at 0.5 s for each ion. Single Ion Monitoring (SIM) mode was used with ion quantification and identification as listed in Table 2. The temperature program was from 90°C to 300°C with a ramp of 5°C/min and from 40°C during 8 min–300°C with a ramp of 40°C/min for PAH and BTEX, respectively. For the other compounds, it was from 90°C to 300°C with a ramp of 50°C/min. Each soil sample was analyzed three times and a blank extraction without soil was inserted in each extraction batch to check for potential contamination during extraction process.

2.5 Quantification and validation method

The concentrations of target compounds were calculated by an external standard calibration method. A calibration curve with five points was obtained using the pure standard in hexane for HAP and BTEX and methanol for alkylphenol, phtalate and TBT. The limits of quantification (LOQ) was calculated based on the signal to noise approach defined in the ICH Harmonized Tripartite Guideline (2005) by dividing the concentration found in extracted samples by a tenth of the signal-to-noise ratio measured in the chromatogram. Finally, the soil contaminant concentrations were calculated by applying a yield factor on each concentration measured after extraction. The extraction yield factors of adsorbed pollutant were calculated by spiking in triplicate a pristine soil in water with a known amount of each contaminant (100 ng per g of soil) and shaking for 24 h to ensure that equilibrium adsorption is reached. After filtration through a nylon membrane (0.2 µm), the liquid fraction was analyzed. The adsorbed amount (deduced by difference between the introduced concentration (100 ng·g^{-1}) and the remaining concentration after shaking) was extracted from the solid fraction by MAE and analyzed to determine the extraction yield. The method was validated by following exactly the same protocol meaning by spiking in triplicated another pristine soil with a known amout of each contaminant. Then the sampled soil was analyzed using the validated method.

2.6 Statistical analysis

Standard deviation, linearity and coefficient of determination were calculated with Excel 2016 datasheet using build-in function (LINEST and STDEV.S) for linear regression. The LOD and LOQ was calculated with the signal to noise approach according to ICH Harmonized Tripartite Guideline (2005). The noise was determinated graphically on the chromatogram for each compounds then the LOQ was calculated as the equivalent concentration of ten times the noise and the LOD as the equivalent concentration of three times the noise.

3 Results and discussion

3.1 Soil characterisation

The soil physico-chemical properties are reported in Table 3. The five soils were very similar in texture: PYZC8, PYZB2, PYZC7,

TABLE 2 Physico-chemical characteristics of the sampled soils and GPS localization. Perc.

Analytes	Quantification ion (m/z)	Identification ion (m/z)
Benzo(k)fluoranthene	252	224, 198
Benzo(b)fluoranthene	252	224, 174
Benzo(a)pyrene	252	225, 126
Indéno(1,2,3-c,d)pyrene	276	248, 138
Benzo(g,h,i)perylene	276	138, 125
Anthracene	178	152, 126
Fluoranthene	202	152, 126
Naphtalene	128	102, 64
Benzene	78	63, 51
Toluene	91	92, 65
Ethylbenzene	91	106, 77
Xylene (o + m + p)	91	106, 77
Diethylphtalate	149	222, 177
Tributyltin cation	269	269, 267, 213
4-Octylphenol	107	206, 96
4-tert-octylphenol	135	136, 107
4-n-nonylphenol	107	220, 77

TABLE 3 Physico-chemical characteristics of the sampled soils and GPS localization. Percentages of organic matter and $CaCO_3$ are expressed as a weight percentage of dry whole solid. Percentages of sand, silt and clay are expressed as weight percentages of dry mineral solid.

	PYZC8	PYZB2	PYZC7	NOZH22	NOZD69
Clay (%)	20	18	20	26	22
Silt (%)	41	44	46	48	51
Sand (%)	39	38	34	26	27
pH	8.4	8.4	8.4	8.4	8.3
$CaCO_3$ (%)	71	73	67	65	44
Cation exchange capacity (cmol kg^{-1})	10.2	8.1	8.6	9.4	13.4
Organic carbon (%)	3.1	2.9	3.2	3.3	3.3
GPS position	49.20889 4.18359	49.21273 4.16566	49.20916 4.18424	49.24698 4.17198	49.2516 4.17986

and NOZH22 were loam, and NOZD69 was silt loam. They displayed a basic pH (≈8.4) which is characteristic of calcareous soils of the Champagne-Ardenne region and in accordance with their high $CaCO_3$ content (between 44% and 73%). Their OC content was relatively high, ranging between 2.9% and 3.3%, and their CEC was comprised between 8.1 and 13.4 $cmol{\cdot}kg^{-1}$. The lack of diversity in soil physico-chemical properties and composition makes extrapolation of data difficult, however a previous study of extractability of organic pollutants using MAE with a wide variety of matrix type has shown that the main soil constituant influencing the extractability of pollutants is total organic carbon (Báez et al., 2003).

3.2 Analytical performance

The performance of the method is summarized in Table 1. Extraction yields ranged from 44% to 96%. The extraction of diethylphtalate, octylphenols, nonylphenols, and toluene was almost quantitative, the one of BTEX compounds ranged from 72% to 96%, while half of the PAH and tributhyltin cation remained adsorbed or lost by degradation during the extraction process. The extraction procedure was intended to be as simple as possible leading in some cases to relatively low extraction yield. However, in each case, the accuracy of the extraction yields was validated by the reproducibility of the extraction allowing an extrapolation of the exact content. In most cases, the LOQ were in the range of a tenth of a $ng{\cdot}g^{-1}$ (few hundreds of ppt). In the case of phenolic compounds, the LOQ were significantly higher, around 50 $ng{\cdot}g^{-1}$. The LOQ values obtained in this paper for the analysis of BTEX and PAH in soils are similar to those reported in previous studies also measured by GC-MS but after solid-phase microextraction (SPME) extraction for BTEX (Franco et al., 2015) or solvent extraction for PAH (Maliszewska-Kordybach et al., 2009). A significant decrease of the detection limits could be reached for alkylphenols by including a derivation step with N-methyltrifluoroacetamide (Zhang et al., 2009) and an alkylation step for tributyltin (Crnoja et al., 2001). Khosravi and Price, 2015 obtained a better quantification limit of less than 1 $pg{\cdot}g^{-1}$ for diethylphtalate using an ASE-SPE-GC-MS method with a higher volume of sample concentrated and transferred in the injector during the analysis. Although other methods have better quantification limits especially when the methods are specifically designed for a single class of compound adding derivation and purification steps (e.g., for alkylphenols) the advantage of our method is the ability to analyze all the target compounds with a small number of preparation steps thus reducing the global cost of analysis. Nevertheless, this strategy leds to a reduction of the performance for some compounds by balancing selectivity and extraction efficiency but allows to reach the quantification limit fixed by the regulation for the whole list of compounds.

3.3 Concentrations of organic contaminants in soil samples

The results of soil analyses are reported in Table 4. PAH and BTEX (except benzene) were identified in all samples at relatively high concentrations, reaching levels higher than 100 $ng{\cdot}g^{-1}$ in the case of benzo(b)fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, and fluoranthene. The total concentration ranged from 406 to 1,237 $ng{\cdot}g^{-1}$ for ∑8PAH and from 21 to 65 $ng{\cdot}g^{-1}$ for ∑BTEX. In France there are no mandatory values defining concentration limits of these pollutants in soil. Concentration limits only exist for ground-water and solid waste. Usually, concentrations are discussed according to the local context or the mean background concentrations. Various field campaigns evidenced the presence of PAH compounds in European soils at amounts depending on the anthropic activities in the area. For example, in Switzerland, concentrations of 98–219 $ng{\cdot}g^{-1}$ were found in different forest sites (Bucheli et al., 2004), whereas these concentrations could reach 575 $ng{\cdot}g^{-1}$ in agricultural soils impacted by anthropic activities (Berset and Holzer, 1995). Sometimes, very high contents of PAH were found like in Poland with concentrations reaching 6,680 $ng{\cdot}g^{-1}$ in soil less than 5 km from the emission source typically industries and urban areas (Maliszewska-Kordybach et al., 2009). In France, a model of the PAH contamination distribution based on 549 uncultivated soil samples throughout the country showed that HAP remained below the detection limits (<5–50 $ng{\cdot}g^{-1}$) in most samples (Villanneau et al., 2013). However, in highly contaminated sites (mining, metallurgy and coal burning activities) individual HAP reached 100–1,000 $ng{\cdot}g^{-1}$. The

TABLE 4 Mean concentrations of organic contaminants measured in soil samples.

Analytes	PYZC8 (ng·g^{-1})	PYZB2 (ng·g^{-1})	NOZH22 (ng·g^{-1})	NOZD69 (ng·g^{-1})	PYZC7 (ng·g^{-1})
Benzo(k)fluoranthene	63	66	44	28	65
Benzo(b)fluoranthene	118	47	59	0.4	177
Benzo(a)pyrene	81	64	40	43	103
Indéno(1,2,3-c,d)pyrene	254	192	141	148	310
Benzo(g,h,i)perylene	105	125	87	58	114
Anthracene	12	15	10	8	36
Fluoranthene	244	235	164	119	429
Naphtalene	0.7 < LOQ	0.8 < LOQ	11	0.30 < LOQ	4 < LOQ
∑8PAH	880	744	558	406	1,237
Benzene	n.d.	n.d.	n.d.	n.d.	n.d.
Toluene	55	51	31	17	5.8
Ethylbenzene	2.21	2.24	1.8	1.3	1.71
Xylene (o)	1.72	1.9	2.6	1.15	4
Xylene (m + p)	6.3	6.64	7.2	6.31	8.96
Diethylphtalate	n.d.	n.d.	n.d.	n.d.	n.d.
Tributyltin cation	n.d.	n.d.	n.d.	n.d.	n.d.
4-Octylphenol	n.d.	n.d.	n.d.	n.d.	n.d.
4-tert-octylphenol	n.d.	n.d.	n.d.	n.d.	n.d.
4-n-nonylphenol	n.d.	n.d.	n.d.	n.d.	n.d.
∑ 4-nonylphenol	n.d.	n.d.	n.d.	n.d.	n.d.
∑ Octylphenols	n.d.	n.d.	n.d.	n.d.	n.d.
∑ Nonylphenols	n.d.	n.d.	n.d.	n.d.	n.d.

n.d., not detected; LOQ, limit of quantification.

authors evidenced that fluoranthene, pyrene and phenanthrene concentrations where geographically correlated with the contamination levels in the northeastern part of France due to historical industrial activities. The concentrations of each PAH in the contaminated soils were between 15 and 35 ng·g^{-1}. In another study, higher values ranging from 190 to 760 ng·g^{-1} were detected in unamended cropland influenced by urban activity and possibly impacted by direct deposition from agricultural engine particles (Gateuille et al., 2014). In the present study, the individual PAH concentrations measured (n.d to 429 ng·g^{-1}) were in the line with European agricultural soils considering its localization (located in the northeastern part of France and near urban and agricultural areas). In agricultural soil, PAH may impact crops growth or germination and invertebrates reproduction. Exposition studies on terrestrial plants (*Sinapsis alba*, *Trifolium pratense*, and *Lolium perenne*) with several PAHs found EC_{20} values from 30 to 650 µg·g^{-1} for the most sensitive values which is above the total of measured PAH (Sverdrup et al., 2003). Survival and reproduction studies of springtail *Folsomia fimetaria L.*, in contaminated soil showed a typical LC_{50} and EC_{50} of 21 and 11 µg·g^{-1} respectively with no-observed-effect concentration of 8.6 µg·g^{-1} for the most sensitive PAH (Sverdrup et al., 2001) which is also above the total of measured PAH.

Concerning the BTEX, few data are available in the literature concerning their concentration into agricultural soils because they are considered to be mainly present in the atmospheric compartment due to their volatility. BTEX are emitted directly by leakage, stock manipulation or sludge application, but they can reach the soil compartment after their emission into the atmosphere by industry, wastewater treatment plant and vehicle exhausts. For benzene, a predicted environmental concentration of 0.02 ng·g^{-1} based on all the releases into the environment was determined in non-contaminated soils or without direct emission at vicinity (EU, 2008). Taking into account the deposition through the atmosphere, the predicted concentrations in agricultural soils increased in the range 1.21–129 ng·g^{-1} (EU, 2008). In the present study, the benzene concentration in the five studied soils was lower than the quantification limit (0.2 ng·g^{-1}) which was consistent with field studies conducted in uncontaminated soils (Ellison et al., 1997). Concerning toluene, modelisation based on emission calculated from traffic and industry was used to estimate its concentration in air, water and soils at local and regional scale (Hansen et al., 2003).

According to this model the expected background concentration of toluene in agricultural was 0.1 ng·g^{-1} and the mean concentration in agricultural soils located near different industrial sites was 7 ng·g^{-1}. In addition, in the case of field studies without any direct pollution context, toluene soil concentrations of 1 ng·g^{-1} and 2.1–5.8 ng·g^{-1} were reported in the Netherland (Sloof and Blokzijl, 1987) and in Poland near petrol station or allotment garden (Zygmunt and Namiesnik, 2001), respectively. In this study, the toluene concentration ranged from 5 to 55 ng·g^{-1}. As for ethylbenzene and xylene data in agricultural soils are very scarce and mostly related to direct spill incident *via* leakage with relative high concentrations in soils. However, using a simple box model, the concentration of ethylbenzene coming from atmospheric depositions was estimated at 0.07 ng·g^{-1} in agricultural soils and until 39 ng·g^{-1} in local areas (EU, 2007). In our studied soils, the ethylbenzene measured concentrations were in the lowest part of this range (around 2 ng·g^{-1}); xylene concentrations were between 1 and 9 ng·g^{-1} which is relatively low compared to the concentrations detected in United States soils ranging from 1 to 190 ng·g^{-1} (Agency for Toxic Substances and Disease Registry (ATSDR), 2007). Thus, according to the cited examples, the measured concentrations of BTEX in the present study is in the same order of level as the measured value in the literature.

The other contaminants, alkylphenols, phthalates and tributyltin were not detected in the studied soil samples. They are surfactants and plasticizers introduced by contaminated wastewater applications or direct deposition from agricultural treatments. Their concentration are thus related to wastewater contamination and agricultural practices. Tributyltin can also be introduced by rainfall leading to very weak concentrations (<1 ng·g^{-1} Sn) (Huang et al., 2004). These compounds are known to persist several days before their degradation in well oxygenated soils (Topp and Starratt, 2000; Hoch, 2001) or deeper migration in soils (Sopheak et al., 2015). As the study focused on topsoil, deeper migration in soil cannot be ruled out. Moreover, this study only focused on regulated pollutants without taking into account their degradation products that may impact the ecosystems. Further experiments will be performed, including these degradation products, to assess their occurrence and impact. Alternatively, other data could indicate a historical contamination such as crop health, ecosystem description, soil fertility or soil microbial content. In any case our study shown that no gradient or trace is left on the topsoil.

4 Conclusion

This study aimed at quantifying multiple organic contaminants targeted by the regulation on industrial wastewater management. The main advantage of the proposed method is to minimize the preparation step of the samples and to allow the compound analysis in an only one analytical method, where other methods need several extraction and derivatization steps (with obvious higher performance) with higher costs. The performances (LOQ) reached by the optimized method meet the legislator requirements. Significant quantities of PAH and BTEX were found in sampled agricultural soils. The mean amounts of these compounds were in agreement with measurements or estimates performed in similar contexts. However, a more detailed work is required to improve the understanding of the contamination scope and location. Investigations are needed to quantify source apportionment of the hydrocarbons found in soils as well as their potential accumulation. In contrast, no plasticizer or surfactant was detected suggesting that degradation or migration efficiently removed the potential soil contamination. Also a more detailed study dedicated to the spreading activities would enable to get a better insight into these processes.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

Formal analysis and investigation by NM; Conceptualization, Methodology, Writing—original draft preparation review and editing: NM, SS, and EG; Funding acquisition, Resources, Supervision: EG; NM, SS, and EG read and approved the final manuscript.

Funding

This work was supported by the “Seine-Normandie” water agency (AESN).

Acknowledgments

The “Association de Suivi des Epandages Agronomiques” (ASAE, M. Robert) is gratefully acknowledged for providing the soil samples. The “Seine-Normandie” water agency (AESN) is gratefully thanked for its financial support.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher’s note

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