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Detection of 13 emerging soil pollutant compounds using a dual extraction method (QuEChERS and solid phase extraction) and a liquid chromatography/mass spectrometry LC-MS/MS method ☆

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Detection of emerging pollutants in soil using a dual extraction of QuEChERS and SPE followed by analysis by LC-MS/MS

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ABSTRACT

Emerging pollutants derived from human and animal sources, are present in soils and pose significant environmental and health impacts, even at low concentrations. Their detection in soil is analytically complex due to soil interference and the rapid degradation of compounds in the matrix. In this study, a protocol was optimized for quantifying hormonal steroids ($n = 7$), human drugs ($n = 3$), and antibiotics ($n = 3$) by a dual-phase extraction using QuEChERS and Solid Phase Extraction (SPE), followed by analysis using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The double extraction phase allows an accurate and effective purification of the target compounds while eliminating the interference in the soil matrix. The method is optimized to detect environmental concentrations of these pollutants, to suit large-scale sampling campaigns and to maintain the efficiency of extraction while reducing analysis time. The limits of detection (LODs) of these compounds ranged between 0.0043 and 0.13 ng/g and recovery rates between 75.9 % and 105.39 %.

- Enhanced Analyte Purification: Implements QuEChERS and SPE for robust removal of matrix interferences, optimizing target compound isolation.
- Precision at Trace Levels: Secures LODs as minimal as 0.0043 ng/g, enabling accurate detection of low-concentration contaminants.
- Adapted for Broad-scale sampling: Modifies extraction and analysis durations to accommodate large-scale environmental assessments.

☆ **Related research article** L.M. Wakim, F. Occelli, M. Paumelle, D. Brousmiche, L. Bouhadj, D. Cuny, A. Descat, C. Lanier, A. Deram, Unveiling the presence of endocrine disrupting chemicals in northern French soils: Land cover variability and implications, Science of The Total Environment, Volume 913, 2024, 169617, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2023.169617.

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Resource availability:	Data will be made available on request.

Method details

Background

The continuous emergence of new pollutants in the environment poses a significant threat to ecosystems and human health, prompting a need for robust analytical methods to detect and quantify these contaminants. Emerging pollutants (EPs) in soils have become a focal point of global concern, given their potential consequences on both terrestrial ecosystems and the well-being of individuals [1]. The term “emerging pollutants” refers to a diverse array of chemicals, encompassing both synthetic and natural compounds, that have been identified in the environment but are not yet subject to routine monitoring [2]. The Food and Agriculture Organization (FAO) [3] has compiled a comprehensive list of EPs, which includes antibiotics, human drugs, hormonal steroids, and other compounds of varying origins. The sources of EPs in soil are diverse, encompassing practices such as wastewater use in agriculture [4], the application of sewage sludge and manure fertilizer, and activities related to concentrated animal feeding operations [5].

Recognizing the urgency of addressing this environmental challenge, Salvia *et al.* (2012) developed a method utilizing liquid chromatography-tandem mass spectrometry (LC-MS/MS) for the simultaneous detection of multiple families of pollutants [6] in complex matrices such as soil. The original method laid a foundation for comprehensive pollutant analysis but necessitated further refinement to accommodate the demands of large-scale sampling campaigns. In response, we have tailored and optimized the method to enhance efficiency, reduce limits of detection (LODs) and limits of quantification (LOQs), and ensure a more accurate representation of environmental pollutant levels. These adaptations are crucial for achieving a method that not only streamlines analysis for extensive soil sampling but also maintains high recovery rates, thus ensuring the reliability of the obtained data.

This method has been optimized to facilitate the detection of various pharmaceuticals and endocrine disruptors in soil samples. This analytical approach targets the identification of antibiotics, including sulfadiazine, roxithromycin, and penicillin G. Additionally, it enables the quantification of the widely used analgesic, paracetamol, and the anti-epileptic drug carbamazepine. The method extends its applicability to the identification of endocrine disruptors, such as the plasticizer bisphenol A, and a spectrum of hormones encompassing testosterone, progesterone, and estrogen variants including 17α-estradiol, 17β-estradiol, estrone, estriol, and the synthetic estrogen 17α-ethinylestradiol. A detailed characterization of the analytical parameters for each component is presented in Table 1.

Materials and reagents

High purity compounds were acquired as analytical standards or Vetranal (V) to spike the soil : 17α-estradiol (V, 98 %), 17β-estradiol (>98 %), estrone (V, >98 %), estriol (V, >95 %), 17α-ethinylestradiol (V, >98 %), Sulfadiazine (V, >98 %), carbamazepine (>99 %), Paracetamol (Acetaminophen-(methyl)) (V, 99 %), Roxithromycin (95–102 %), Penicillin G (potassium salt, V > 98 %), Testosterone (purum, >99 %), progesterone (V, 99. 5 %) and Bisphenol A (>99 %) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France).

Table 1
Physiochemical properties of the selected EPs and their families.

Category	Family	Compound	Formula	Molecular mass (g/mol)	pKa
Antibiotics	Sulfonamide	Sulfadiazine	$C_{10}H_{10}N_4O_2S$	250.28	6.50
	Macrolides	Roxithromycin	$C_{41}H_{76}N_2O_{15}$	837.05	9.17
	β-Lactam	Penicillin G	$C_{16}H_{18}N_2O_4S$	334.40	2.80
Human drugs	Analgesic	Paracetamol	$C_8H_9NO_2$	151.16	9.90
	Anti-epileptics	Carbamazepine	$C_{15}H_{12}N_2O$	236.27	13.90
Endocrine disruptors	Plasticizer	Bisphenol A	$C_{15}H_{16}O_2$	228.29	9.59
	Androgens	Testosterone	$C_{19}H_{28}O_2$	288.43	10.00
	Progestogens	Progesterone	$C_{21}H_{30}O_2$	314.46	–
	Estrogens	17α-estradiol (αE2)	$C_{18}H_{24}O_2$	272.38	10.70
		17β-estradiol (βE2)	$C_{18}H_{24}O_2$	272.40	10.71
		Estrone (E1)	$C_{18}H_{22}O_2$	270.37	10.77
		Estriol (E3)	$C_{18}H_{24}O_3$	288.38	10.40
		17α-ethinylestradiol (EE2)	$C_{20}H_{24}O_2$	296.40	10.05

Individual stock solutions were prepared at concentrations of 1 mM in methanol (MeOH), except for paracetamol in water, and stored at −23 °C. Working solutions were prepared by the adequate mixture and dilution of the stock solutions.

Compounds were also purchased deuterated to serve as internal standards (IS): 17β-estradiol-2,4,16,16,17-d5 from Sigma-Aldrich, Sulfadiazine-d4, Carbamazepine-d10, Roxithromycin (Erythromycin-(N-methyl-13C, d3)), Testosterone- 2,2,4,6,6-d5, and Progesterone-2,2,4,6,6,17α,21,21,21-d9 were purchased from C/D/N Isotope (Cluzeau, Sainte Foy La Grande, France). Naphthol was used as an IS for Bisphenol A and was purchased from Sigma-Aldrich.

A stock solution was prepared for deuterated compounds at a concentration of 1 mM in MeOH (in water for paracetamol-d3) and stored at −23 °C. The working solutions were then prepared by the mixture of the stock solution and adequate dilution.

For extraction in SPE, SAX cartridges (500 mg, 3 mL) were purchased from Agilent technologies and STRATA-X cartridges (200 mg, 3 mL) were purchased from Phenomenex.

For liquid chromatography, columns were purchased from Agilent technologies: Zorbac Eclipse XDB C_{18} (2.1 × 100 mm, 3.5 µm) and Kinetex Biphenyl (2.1 × 100 mm, 2.6 µm). For each, a pre-column (AF0–8782) and its 2.1 mm holder (AF0–9000) were purchased from Phenomenex.

The methanol (MeOH) was purchased from Fisher Chemical and the acetonitrile (LC-MS grade) was purchased from VWR chemicals. MilliQ water was provided by a system of MilliQ water of Millipore. The monohydrated citric acid and the ammonium fluoride (NH_4F) were purchased from Fisher scientific, as for magnesium sulfate ($MgSO_4$) and sodium acetate ($C_2H_3NaO_2$), they were purchased from Agilent technologies.

Soil preparation

For the preparation of this protocol, a loamy soil was collected from a public garden in Lille, France at a depth between 10 and 20 cm. All samples were made in triplicates.

The samples were air dry and sieved through a 3 mm sieve to remove large particles. They were then crushed in a grinder and passed through a 0.63 mm sieve to obtain a homogeneous sample. Samples were stored at −23 °C before analysis. It is advisable to refrain from extending the sample storage duration beyond one week prior to the commencement of the analysis to mitigate potential alterations or degradation of sample integrity.

5 g of soil were placed in a 50 mL centrifuge tube and deuterated compounds were added to 50 µL at 200 nM (range between 31×10^3 and 168.2×10^3 ng/L depending on the compound) in the sample. The mixture was homogenized by shaking the tube on a vortex mixer.

For the validation of the method, the soil was spiked with 50 µL of a solution of the 13 molecules at 150 nM each with the compounds (range between 22.6×10^3 and 125.5×10^3 ng/L depending on the M of the compounds).

QuEChERS (Quick, easy, cheap, effective, rugged, safe extraction)

The spiked soil (5 g) was mixed with 10 mL of MilliQ water and 15 mL of acetonitrile for 30 s using a vortex mixer. A mix of 6 g of magnesium sulfate and 1.5 g of sodium acetate was then added and mixed for another 30 s with the vortex. The mixture was centrifugated for 3 min at 750 rpm, and 2 mL of the upper solution was collected into a 15 mL tube and dried under a nitrogen flow at 40 °C. The dried residue was dissolved in 10 mL 0.04 M citric acid/MeOH 97/3 (pH=2.5). This method is illustrated in Fig. 1.

Extraction/purification by solid-phase extraction (SPE)

The second extraction phase utilizes two distinct SPE cartridges, SAX and StrataX, to purify QuEChERS residues and enhance the selective extraction of target compounds, thus increasing both selectivity and efficiency [6]. The SAX cartridge, featuring a

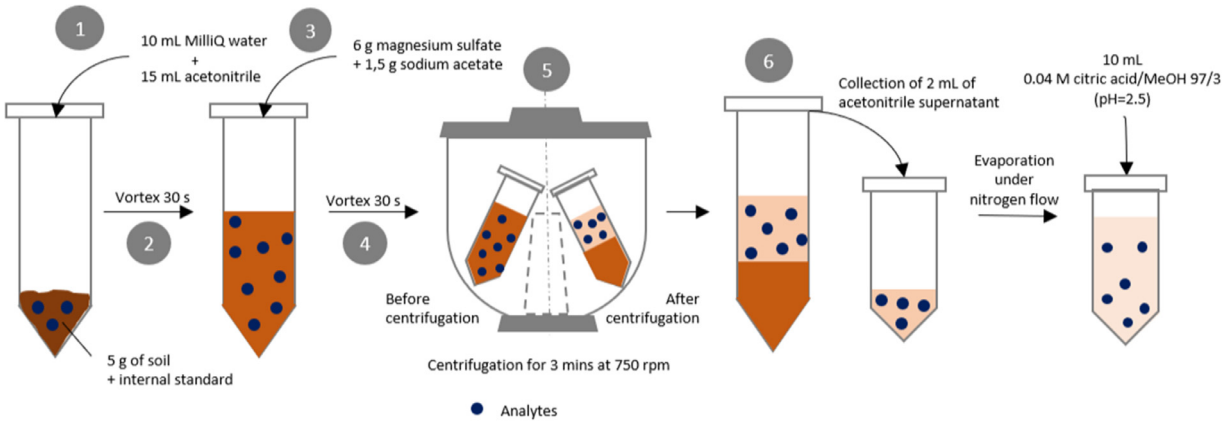

Fig. 1. Illustration of the QuEChERS method for extraction in soil matrix.

quaternary ammonium bonded phase on a silica matrix and a strong anion-exchange phase, effectively removes negatively charged matrix components, like humic and fulvic acids from soil extracts. The SAX cartridge ensures the retention of strong anions and the elution of the target analytes that are non-ionized at a pH of 2.5 given their pKa (Table 1).

Following this, the StrataX cartridge, characterized by its styrene-divinylbenzene and pyrrolidone copolymer structure, selectively retains both hydrophobic and moderately polar compounds. This includes hydrophobic steroids and non-polar substances such as bisphenol A and carbamazepine, through mechanisms of non-polar interactions and size exclusion. The StrataX cartridge effectively discards the most hydrophilic compounds while retaining the targeted analytes, thus ensuring a high degree of extraction with acceptable recovery by effectively separating the target compounds from highly hydrophilic non-target substances.

The SAX cartridge was conditioned with 5 mL MeOH and 5 mL 0.04 M citric acid at approximately 4 mL/min. The sample from the QuEChERS extraction was ultrasonicated at 25 ˚C for an hour for better dissolution and then was introduced to the SAX cartridge at around 1 mL/min. The untargeted compounds which were negatively charged at the acid pH were retained by the cartridge whereas neutral or cationic targeted compounds were eluted.

The StrataX cartridge was conditioned as described for the SAX cartridge. The extract from SAX was then introduced to the StrataX cartridge at around 1 mL/min. The compounds were retained by the StrataX. The cartridge was then washed with 2 mL sodium acetate 0.1 M (pH=8.9), 2 mL of 0.04 M citric acid and 2 mL of MilliQ water at 5 mL/min. The targeted compounds were then eluted by adding 10 mL of MeOH to the cartridge at 1 mL/min. The recovered extract was then evaporated to dryness under a gentle stream of nitrogen at a temperature of 40 ˚C. Prior to LC-MS/MS analysis, the dry residue was dissolved in 200 µL of 95/5 H_2O/MeOH and mixed for 20 s. The Fig. 2 below shows an illustration of this experimental protocol.

Analysis by liquid chromatography coupled with mass spectrometry (LC-MS/MS)

In the phase of LC-MS/MS analysis, two distinct methods were employed utilizing a UFLC-20XR Shimadzu system equipped with a degasser, binary pump, autosampler, and a column oven, coupled with a 5500 QTrap triple quadrupole mass spectrometer (Sciex, France) featuring a turbo-electro-spray ion source (turbo-ESI).

Method A: analysis of estrogens and bisphenol A. The Zorbax Eclipse XDB C_{18} column (100 mm x 2.1 mm, 3.5 µm) with a pre-column was employed. The mobile phases consisted of (A) MilliQ water with 0.05 mM ammonium fluoride (NH_4F) and (B) a mixture of 50/50 ACN/MeOH. NH_4F was added to enhance the signal for estrogen detection [7].

Method B: analysis of sulfadiazine, roxithromycin, penicillin G, paracetamol, carbamazepine, testosterone, and progesterone. The Kinetex Biphenyl column (100 mm × 2.1 mm, 2.6 µm) with the same pre-column was used. Mobile phases included (A) 0.01 % formic acid solution in MilliQ water (pH = 3.3) and (B)MeOH.

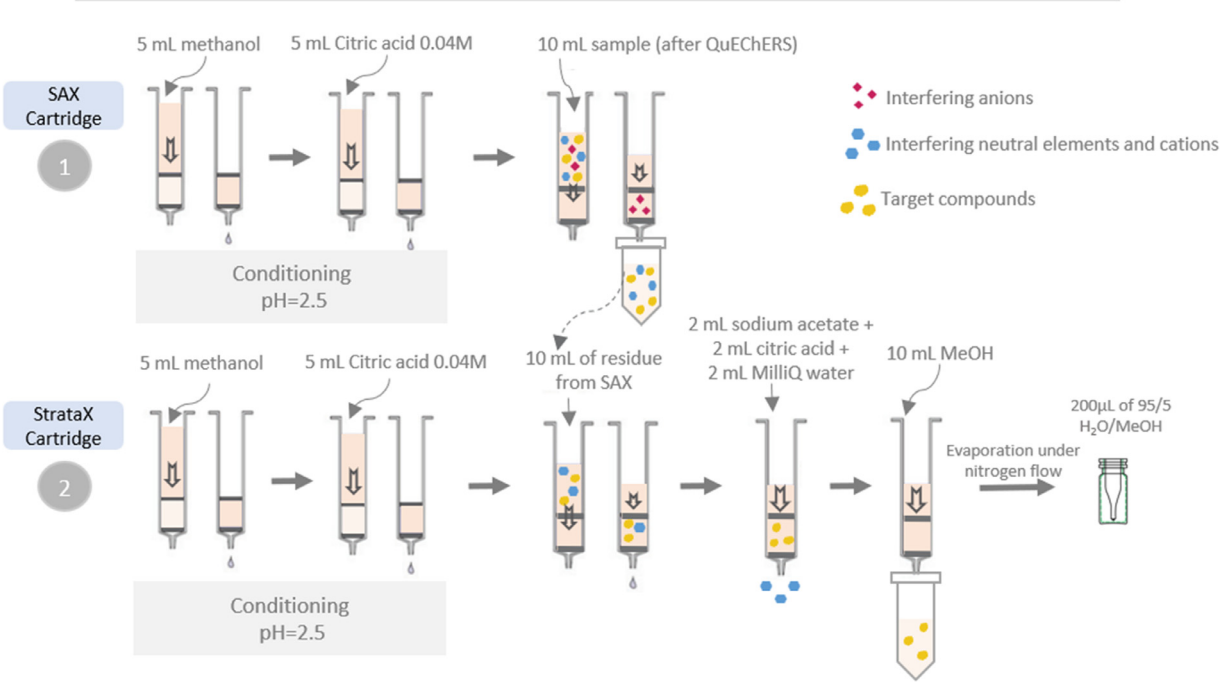

Fig. 2. Illustration of the SPE method for extraction/purification in soil matrix.

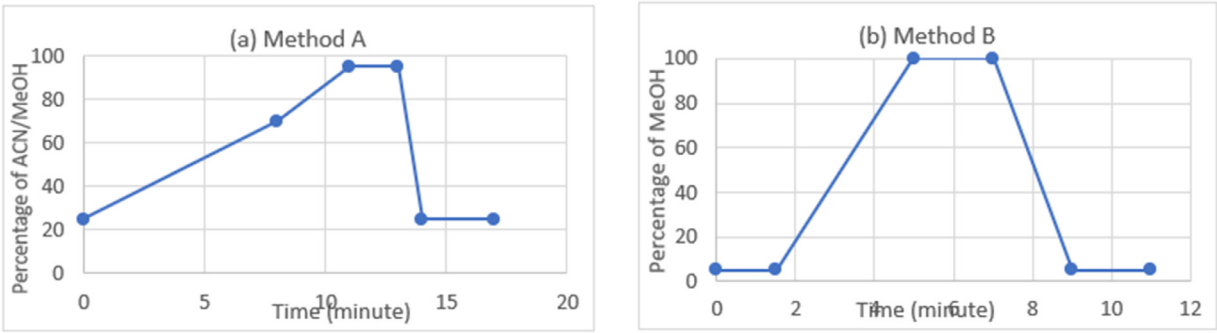

Fig. 3. Gradient used for Method A (a) and Method B (b).

Table 2
Parameters of ionization optimization.

Parameter	Method A (ESI-)	Method B (ESI+)
Gas 1 nebulization (air)	45 psi	45 psi
Gas 2 (Gaz turbo) (air)	45 psi	45 psi
Curtain Gas (CUR) (nitrogen)	20 psi	25 psi
Temperature (TEM)	500 °C	500 °C
Ion spray voltage (S)	−4500 V	5500 V

Chromatographic separation was achieved with the two different columns, maintaining an oven temperature of 50 °C, a flow rate of 0.3 mL/min, and an injection volume of $V = 5$ µL. Method-specific gradients were optimized, as depicted in Fig. 3, with both methods featuring a 17-minutes gradient for method A and an 11-minutes gradient for method B.

Detection was performed in multiple reactions monitoring (MRM) mode. The ionization parameters were optimized, with positive and negative ionization modes based on the structural properties of the analytes. With a flow rate of 0.3 mL/min, and 50 % A-phase and 50 % B-phase, the source parameters for the negative and positive modes were optimized and are presented in Table 2.

The adequate product ions and collision energies (CE) were investigated. Entrance Potential (EP) for positively ionized molecules is +10 V and for negatively ionized molecules is −10 V. Table 3 provides comprehensive information on the precursor ions, product ions, collision energies (CE), declustering potentials (DP), and collision cell exit potentials (CXP) for each compound, including their Internal Standards (IS). The optimized parameters for compounds analyzed in both positive (ESI+) and negative (ESI-) ionization

Table 3
Retention time and MRM parameters of the 13 compounds in both positive and negative ionization mode.

Compound	t_R (min)	Precursor ion > product ion (CE (eV))	Potential DP (V)	Collision cell exit potential CXP (V)
ESI +				
Paracetamol	2.87	152>110 (24) and 152>93 (30)	65	15
Paracetamol-d_3	2.86	155>111 (24)	65	15
Sulfadiazine	4.68 (1′)	251>156 (21) and 251>92 (38)	65	13; 17
Sulfadiazine(benzene—d_4)	4.67	255>160 (23)	100	15
Penicillin G	5.69 (2′)	335>217 (22) and 335>160 (20)	180	25
Penicillin G-d_5	5.70	340>160 (26)	65	19
Roxithromycin	5.78 (3′)	837>679 (28) and 837>158 (44)	65	26
Erythromycin-(N-methyl-^{13}C), d_3	5.76	844>686 (30)	100	28
Carbamazepine	5.93 (4′)	237>194 (30) and 237>165 (60)	65	22
Carbamazepine-d_{10}	5.91	247>204 (30)	140	26
Testosterone	6.35 (5′)	289>97 (29) and 289>109 (33)	65	15
Testosterone-2,2,4,6,6-d_5	6.34	292>97 (29)	65	15
Progesterone	6.76 (6′)	315>97 (30) and 315>109 (33)	65	13
Progesterone-2,2,4,6,6,17α,21,21,21-d_9	6.74	324>113 (30)	110	15
ESI −				
Estriol	4.22 (1)	287>145 (−54) and 287>171 (−49)	−180	−7; −20
Bisphenol A	6.8 (2)	227>133 (−34) and 227>117 (−65)	−140	−12
Naphthol	5.86	143>115 (−40)	−110	−15
17β-estradiol	7.55 (3)	271>145 (−56) and 271>183 (−51)	−200	−18
17β-estradiol-d_5	7.55	276>147 (−53)	−190	−15
17α-estradiol	7.96 (4)	271>145 (−50) and 271>143 (−72)	−213	−15
17α- ethinylestradiol	7.97 (5)	295>145 (−50) and 295>143 (−71)	−120	−19
Estrone	8.09 (6)	269>145 (−50) and 269>143 (−72)	−100	−16

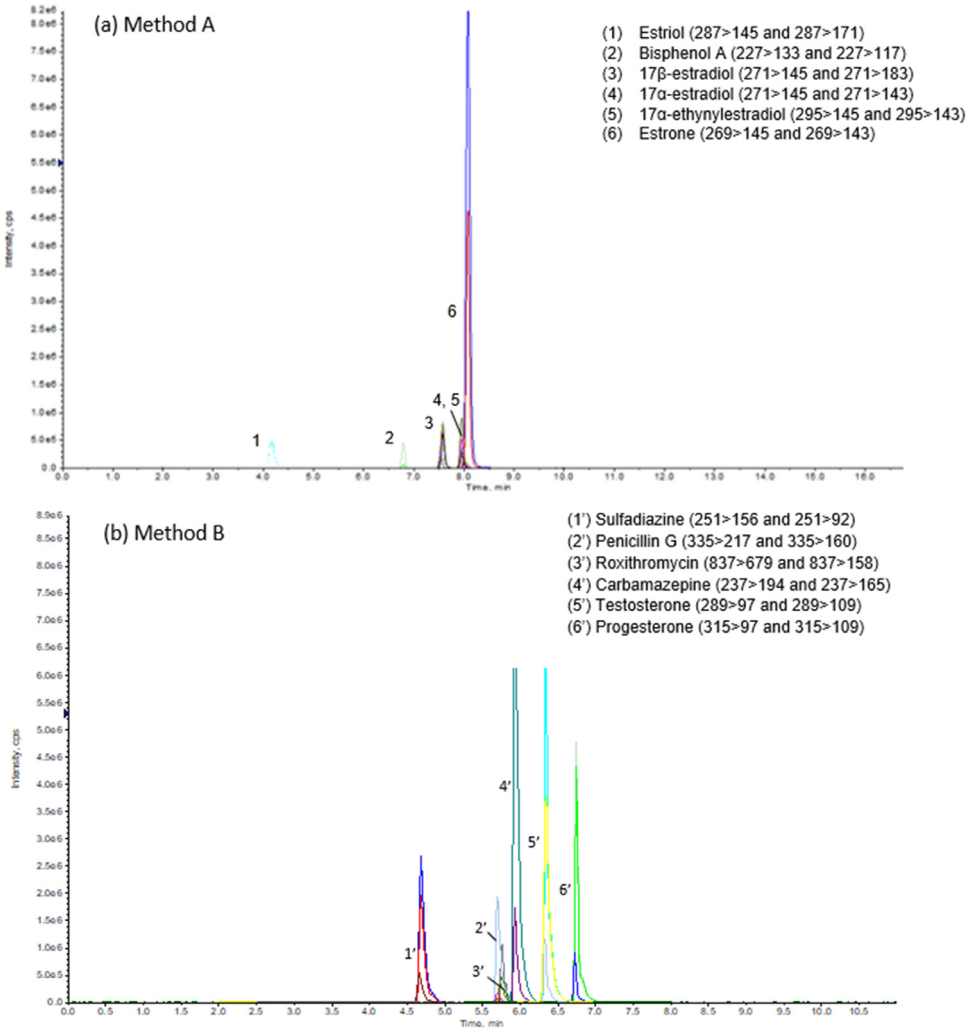

Fig. 4. Chromatogram of a calibration point at 150 nM in MeOH for Method A (a) and Method B (b).

modes were outlined. Additionally, the retention times in minutes were also specified for both the target compounds and their corresponding IS.

The data was analyzed using the Analyst 1.7.2 software. The chromatograms (Fig. 4) represent the separation of the compounds with their respective IS, for method A in (a) and for method B in (b) with their retention time.

In the chromatogram generated by method B (Fig. 4), the signal corresponding to the detection of paracetamol exhibited a small intensity compared to the other compounds. This divergence was attributed to the solubility characteristics of paracetamol, which demonstrated better solubility in water compared to the MeOH solvent used for dissolving the other compounds. To address this, a calibration curve for paracetamol was established in water, with the same concentrations as the remaining compounds. Fig. 5 presents the calibration point at 150 nM (22.6×10^3 ng/L) for paracetamol, with an enhanced signal detected for the analyte. The use of H_2O/MeOH 95/5 before introduction into the LC-MS/MS allows the paracetamol analyte and its internal standard to be detectable.

Method validation

- Calibration curve

The calibration curve was generated using solutions of varying concentrations, specifically 0.5, 5, 25, 50, 75, 100, 150, and 250 nM (for estrone for example 135, 1350, 6750, 13,500, 20,250, 27,000, 40,500 and 67,500 ng/L). The concentration of the internal standard (IS) was consistently set at 150 nM (ranging between 22.6×10^3 ng/L for paracetamol and 125.55×10^3 ng/L for roxithromycin) across all tested solutions. The calibration process involved creating a mixture of the target compounds in MeOH, with the exception of paracetamol, for which a distinct calibration curve was prepared using water as the solvent.

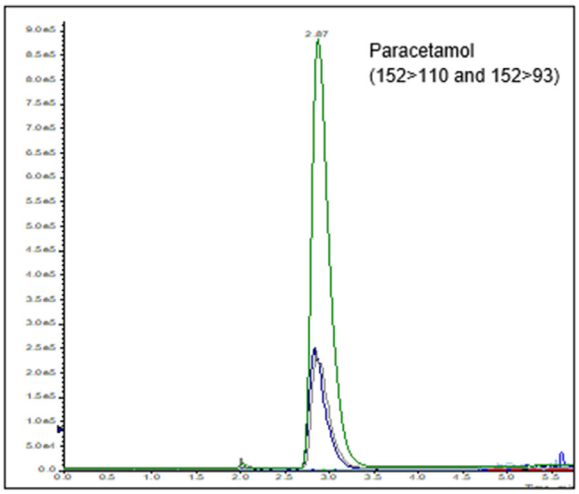

Fig. 5. Chromatogram of a calibration point at 150 nM (22.6×10^3 ng/L) for paracetamol in water using method B.

- LODs and LOQs

The soil extracts were spiked with a methanol solution containing the 13 compounds at 150 nM each in order to evaluate the LODs, LOQs, the matrix effect and the recovery. The LODs and LOQs were established for each analyte through a signal-to-noise ratio (S/N) approach, employing thresholds of 3 for LODs and 10 for LOQs. Rigorous validation was conducted using loam soil collected in Lille, France.

In this study, LODs values ranged from 0.001 to 0.13 ng/g, and LOQs values varied from 0.0043 ng/g for estrone (E1) to 0.43 ng/g for 17β-estradiol (βE2). These findings are detailed in Table 4 for all compounds. Notably, the achieved LODs and LOQs values in our method are markedly lower than those reported in the literature for comparable LC-MS/MS techniques. Specifically, our results surpass the sensitivities reported by Ferhi *et al.* [8] (LODs: 2.1–65.3 ng/g) and Nieto *et al.* [9] (LODs: 14–32 ng/g). The sensitivity of our method aligns more closely with the LODs ranges reported by Ma *et al.* in 2018 [10] and Salvia *et al.* [6], demonstrating superior analytical performance with a range of 0.001–0.462 ng/g in Ma *et al.* (2018) and of 0.006–7 ng/g in Salvia *et al.* (2012), all measured in soil samples.

- Matrix effect

During soil analysis, the presence of a matrix effect is commonly mentioned. In fact, at the electrospray interface, the matrix's interferents are in direct competition with the compounds being studied, causing either a signal decrease or an increase that leads to inaccurate results. The signal in the matrix S(matrix) was compared to a standard signal in solvent S(solvent) containing the same compound concentrations. The matrix effect was then identified using the relationship shown below:

$$\text{Matrix effect}(\%) = \left(\frac{S(matrix) - S(blank)}{S(solvent)} - 1 \right) \times 100$$

where S(blank) corresponds to the signal of the non-spiked extract of soil.

Table 4
LODs and LOQs of the 13 EPs, matrix effect and efficiency extraction.

Compounds	LODs (ng/g)	LOQs (ng/g)	Recovery (%)	Matrix effect (%)	RSD (%)
Sulfadiazine	0.004	0.015	97.18	−6.17	26
Roxithromycin	0.045	0.15	105.39	6.12	47
Penicillin G	0.029	0.097	75.90	−7.77	32
Carbamazepine	0.002	0.009	76.81	−9.97	21
Paracetamol	0.036	0.12	99.72*	−28.53	28
Testosterone	0.003	0.009	100.45	−15.26	22
Progesterone	0.003	0.011	86.25	−8.17	17
Bisphenol A	0.0063	0.21	84.27	−6.85	12
Estrone	0.001	0.004	91.19	−4.83	6
17α-estradiol	0.016	0.051	99.29	3.48	17
17α- ethinylestradiol	0.0057	0.19	91.68	31.8	23
Estriol	0.0043	0.14	79.49	−5.21	29
17β-estradiol	0.13	0.43	98.87	−1.66	22

* Recovery calculated without IS.

Table 5
Concentration of the 13 EPs in different soil samples (ng/g).

Compounds	Soil A	Soil B	Soil C	Soil D
Sulfadiazine	<LOQs	<LOQs	<LOQs	<LOQs
Roxithromycin	11.60	<LOQs	1.36	<LOQs
Penicillin G	0.23	4.01	1.45	5.96
Carbamazepine	<LOQs	<LOQs	<LOQs	<LOQs
Testosterone	<LOQs	<LOQs	<LOQs	<LOQs
Progesterone	0.48	0.32	0.82	0.95
Paracetamol	43.55	11.91	9.89	7.36
Bisphenol A	36.4	34.00	19.88	34.8
Estrone	0.35	0.43	0.38	0.39
17α-estradiol	0.22	0.03	0.04	<LOQs
17α-ethinylestradiol	79.6	0.52	0.45	0.18
Estriol	0.06	<LOQs	0.04	0.12
17β-estradiol	0.11	0.11	<LOQs	0.07

Matrix effects were assessed for each compound, revealing variations in their impact on the analytical signal. The calculated matrix effects exhibited a diverse range among the targeted compounds, spanning from −28 % for paracetamol to +31 % for 17α-ethinylestradiol (Table 4).

- Recovery and precision

The recovery was evaluated by calculating the peak area of spiked soil samples at 150 nM before extraction to the peak area of spiked soil after extraction with their IS. The recovery rates varied from 75.9 % for penicillin G, indicating a slight underestimation of the concentration, to 105.39 % for roxithromycin, demonstrating a slightly higher recovery. The recovery rate was calculated without IS for the paracetamol.

The precision for repeatability is evaluated by calculating the relative standard deviation (RSD,%), at 150 nM. The RSD values, indicative of the degree of variability in repeated measurements, exhibited a range from 6 % to 47 %. These values, presented in Table 4, encompass the variability observed across the entire spectrum of targeted compounds, providing a comprehensive understanding of the method's precision.

Application of the method

The QuEChERS/SPE/LC-MS/MS method was utilized to analyze soil samples collected from various locations in the Lille region of France. Four samples of soil were collected from different land covers extracting and mixing the top 20 cm of soil. The samples (A, B, C, and D) were collected from different locations including a botanical garden, a private residential garden, a university campus sidewalk, and a public garden near a residential area, respectively. The soil samples were properly prepared and analyzed using the dual extraction and LC-MS/MS analysis protocol in triplicates.

Among the 13 target compounds analyzed, 10 were detected in the collected urban soil samples. The analytical results are summarized in Table 5, which indicates the widespread occurrence of emerging pollutants in trace amounts across the sampled soils. Notably, Penicillin G, progesterone, paracetamol, bisphenol A, estrone, and 17α-ethinylestradiol were present in all samples. Particularly, Sample A exhibited the highest concentrations of synthetic estrogens (79.6 ng/g), roxithromycin (11.6 ng/g), bisphenol A (36.4 ng/g), and paracetamol (43.55 ng/g). Conversely, sulfadiazine, carbamazepine, and testosterone were not detected in any samples.

Bisphenol A and paracetamol were found in significantly high concentrations, with bisphenol A ranging from 19.88 to 36.4 ng/g and paracetamol from 7.36 to 43.55 ng/g. Lower concentrations were observed for the antibiotics roxithromycin and penicillin G, underscoring the variable persistence and deposition of pharmaceutical compounds in urban environments.

Conclusion

The experimental protocol for the detection of EPs in soil represents a robust and efficient approach for the simultaneous detection of these EPs in a complex soil matrix, while maintaining low detection limits and high efficiency. The integration of a dual extraction method, combining QuEChERS and solid phase extraction (SPE) using two cartridges, enhances the selectivity and sensitivity of the process. Subsequent analysis by LC-MS/MS ensures simultaneous detection of multiple compounds, while enabling compound separation and high detectability. The method's low detection limit enables environmental concentrations to be identified in an efficient time, making it equally suitable for large-scale sampling campaigns. Noteworthy time optimization, especially in the evaporation phases, has been achieved throughout the protocol development. This protocol is a valuable tool for tackling the challenges associated with the complex nature of soil, offering a reliable means of detecting and quantifying emerging pollutants in environmental matrices.

Ethics statements

N.A.

CRediT author statement

Wakim Lara Maria: Conceptualization, Methodology, writing original draft. **Descat Amandine**: Validity tests, methodology, reviewing and editing. **Deram Annabelle**: Supervision, reviewing and editing. **Occelli Florent**: Supervision, reviewing and editing. **Goossens Jean-François**: Supervision, reviewing and editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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