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Unveiling the presence of endocrine disrupting chemicals in northern French soils: Land cover variability and implications

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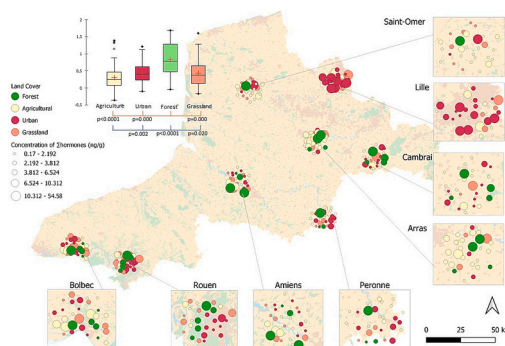
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HIGHLIGHTS

- The first large-scale European campaign detecting emerging pollutants in soils.
- Eight endocrine disrupting chemicals (EDCs) were identified in 240 soil samples.
- EDCs show a heterogeneous spatial distribution across land covers.
- Forest lands exhibit high 17 α -ethinylestradiol and 17 β -estradiol concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Endocrine disrupting chemicals (EDCs) are chemicals that can be found in the environment and have adverse effects on human health by mimicking, perturbing and blocking the function of hormones. They are commonly studied in water surfaces, rarely in soils, although it can be an important source of their presence in the environment. Their detection in soils is analytically challenging to quantify, hence the lack of known background concentrations found in the literature. This scientific research aimed to detect EDCs in soils by analyzing 240 soil samples using an optimized protocol of double extraction and analysis using liquid chromatography coupled to mass spectrometry. The optimized protocol allowed for very sensitive detection of the targeted compounds. The results showed a high concentration of 29.391 ng/g of 17 β -estradiol in soils and 47.16 ng/g for 17 α -ethinylestradiol. Testosterone and Progesterone were detected at a highest of 1.02 and 6.58 ng/g, respectively. The Σ EDCs which included estrogens, progesterone, testosterone and Bisphenol A was found at an average of 22.72 \pm 35.46 ng/g in the study area. The results of this campaign showed a heterogeneous geographic distribution of the EDCs compounds in the different zones of study. Additionally, the study conducted a comparison of the

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concentration of EDCs in different land covers including urban areas, agricultural lands, grasslands and forests. We observed a significant difference between forests and other land covers ($p < 0.0001$) for 17 α -ethinylestradiol, estradiol, and progesterone. This presence of EDCs in forest lands is not yet understood and requires further studies concerning its origins, its fate and its effect on human health. This study is the first large-scale sampling campaign targeting EDCs in soils in Europe and the second in the world. It is also the first to assess the concentrations of these compounds based on different land covers.

1. Introduction

The endocrine system is responsible for the regulation of hormones in the body (Monneret, 2017). By mimicking, disrupting, and blocking the activity of hormones, the endocrine disrupting chemicals (EDCs) can prevent the endocrine system from operating normally (Matsui, 2008). This can have adverse effects on the synthesis, metabolism, and uptake or release of natural hormones, leading to developmental, reproductive, neurological, and immune issues in humans. Natural sex hormones including androgens, estrogens, and progestogens are essential for controlling the endocrine system in both humans and animals. However, when released into the environment, these hormones may behave as EDCs (Varticovski et al., 2022).

The World Health Organization (WHO) acknowledges that EDCs are potentially harmful to ecosystems, wildlife, and human health (Bergman et al., 2012). EDCs may have a detrimental effect on crop development, nutrient cycling, and microbial populations in the soil (Ying and Kookana, 2005), (Card, 2011). Some EDCs can build up in the food chain and endanger human health (Connolly, 2009). In fact, during the past few decades, endocrine-related diseases like cancer, neurobehavioral disorders, genital abnormalities, diabetes (Wang et al., 2019), and problems with brain function have increased globally (Bergman et al., 2012). EDCs have a high affinity for endocrine receptors, leading to significant estrogenic activity, even at low concentrations, and pose a significant biological risk (Pollard and Morra, 2017). They adversely affect aquatic organisms (Leet et al., 2011) (Hakk et al., 2005) and a wide range of animals (Wojnarowski et al., 2021), and in humans, they are linked to breast cancer, infertility, and reproductive issues (Bilal et al., 2019). WHO has classified estrogen as a Group 1 carcinogen (Damstra et al., 2002), where estradiol was linked to breast, ovarian and lung cancer (Orzolek et al., 2022) and exposure to estrogens and progesterone as a hormonal therapy is also linked to a high risk of ovarian cancer (National cancer institute, 2015). Long-term exposure to low concentrations of synthetic estrogens affects gene expression and parasite intensity in trout, while adverse effects on aquatic organisms can occur at low concentrations (Rehberger et al., 2020). EDCs also include synthetic substances like pesticides, herbicides, plasticizers, and polycyclic aromatic hydrocarbons (PAHs), and natural chemicals such as sex hormones that are present in both human and animal food (Diamanti-Kandarakis et al., 2009). Exposure to plasticizers is associated with infertility and cancer (Konieczna et al., 2015), while hormonal exposure affects sexual orientation and behavior (Reinisch et al., 2017), (Hines et al., 2015).

These EDCs can be found in various sources of the environment, including soils. A significant source of estrogen in the environment is livestock, which is thought to excrete 83,000 kg/year in the United States and the European Union (Adeel et al., 2017), more than twice as much as the entire human discharge (Shrestha et al., 2012). Animal manure or sludge bio-solids are frequently used in modern agriculture as fertilizers (Xuan et al., 2008), which may introduce EDCs into the soil (Lee et al., 2003), as well as through wastewater treatment plants that cannot completely eliminate them (du Plessis et al., 2023). Bisphenol A (BPA), an EDCs found in plastic products, especially food containers (Kim et al., 2018), has an estimated global production of 10 million tons in 2022 (Huelsmann et al., 2021). It is released into the soil and water during the production process and is currently restricted in plastic bottles and packaging in Europe due to its potentially harmful effects

(Mahamuni and Shrinithiviahshini, 2017). BPA can also leach into soils from landfills where it is disposed of a part of plastic waste, in addition to its release from wastewater (Song et al., 2014) and agricultural practices (Xu et al., 2021).

Over the last decade, more and more research has been devoted to studying the presence of EDCs in soils. The main objective of these studies has been to address the challenges associated with detecting these compounds in soil, given its complex matrix nature with various potential interferences that can influence accurate measurements, particularly at low concentrations (Salvia, 2013). Consequently, research has sought to identify suitable analytical methods capable of detecting EDCs at their lowest concentrations, while studying their sorption and desorption in soils (Dai et al., 2022), as well as their fate. Progesterone, androstenedione and estrone are found to accumulate relatively easily in soils (Zhang et al., 2015b).

Despite the importance of these methodological breakthroughs, there are still very few large-scale studies aimed at monitoring and detecting the presence of EDCs in soils (Yang et al., 2021a). This lack of data is striking in comparison with water bodies, where their presence is detected on a national level in many countries (Adeel et al., 2017). Among the 20 studies found in the literature, only one describes EDCs in a large area (Yang et al., 2021a). Moreover, the majority of these studies primarily concentrated on agricultural soils and none considered the spatial distribution of EDCs for diverse land use. They finally focus on a few EDCs and not on mixtures (hormones and BPA). This scarcity of in-depth research raises concerns about the extent of our understanding of the presence of EDCs in the environment.

The complexity of establishing regulations at both national and international levels is well explained by these factors. Regulations for EDCs concentrations in soils are unavailable to date. However, in relation to water intended for human consumption, the European Union has set a maximum limit of 0.035 ng/L for 17 α -ethinylestradiol and 0.4 ng/L for 17 β -estradiol (de A. Pismel et al., 2021). In order to develop effective environmental management policies, a comprehensive understanding of pollutants in soils is essential. This includes knowledge of their presence, spatial distribution, particularly across various land use types, and their potential combinations as mixtures. To fill this gap, our study aims to characterize the spatial distribution of EDCs mixture in soils at a large scale across multiple land covers and landscapes. 240 soil samples were collected in the northern region of France, where the detection of EDCs in soils has never been explored before. It is actually the first study to conduct a large screening in soils of EDCs in Europe. Eight EDCs including hormones (estrogens, progesterone, testosterone) and BPA were analyzed with the use of an optimized multi-family analytical protocol. Their presence and concentration in soils were described across different regions and land use.

2. Materials & methods

2.1. Literature review

To perform a systematic review of the current knowledge on the concentrations of these pollutants in soils, we searched PubMed and Google Scholar, with the following query: [Soil] AND [Estrogen(s) OR hormones OR Bisphenol A OR endocrine disrupting OR EDC(s)]. All studies published in English or French, between 2000 and 2023 were considered during the first step.

The search conducted on May 30, 2023, produced a substantial number of results related to the topic. Specifically, a total of 943,167 results were found on PubMed, while Google Scholar yielded 18,100 results between the years 2000 and 2023. To ensure the relevance of the selected studies, we screened them using predefined inclusion criteria. Studies that did not directly investigate soil, such as those focusing on sediment, manure, sludges, biosolids, water forms, and surfaces, were excluded. Additionally, studies that involved artificially spiking soil samples with EDCs were also removed from consideration. After applying these filters, we identified and included 20 studies that provided a comprehensive analysis of the actual concentrations of EDCs present in the soil. Additional searches on Web of Science and Science Direct did not reveal any new study.

2.2. Sampling sites

A total of 240 soil samples were collected in the period between 25 April and 18 October 2022, from 8 distinct zones of 4 departments in northern France: Nord, Somme, Pas-de-Calais and Seine-Maritime. Within the study area, the sampling zones are situated within the largest agglomerations of the region, where diverse landscapes are evident due to varying land use patterns. They are areas of high land use diversity and a large history of industrial activities. In each of the eight zones, 30 sites were selected.

Hexagonal meshes were created in the selected areas representing an area of around 260 km² with an average distance between sites of 1.8 km (see Supplementary materials 1). Inside each mesh a site was selected, considering their distance to the center of the mesh and their land cover. The latest was assessed using the database of Corine Land Cover (CLC) found in open access from the Copernicus Land Monitoring Service website. The sites inside these zones showed diverse profiles of these repartitions in land covers that reflect an overview of the whole research region, which is represented by 55 % of agricultural areas, 21 % of

artificial or urban surfaces, and 19 % of forest and natural areas. The selection was also based on areas of potential sources of EDCs such as farms, grazing sites, agricultural lands with biosolid applications and sites of previous industrial activities, which made it difficult to target the center of the mesh in the selection.

Fig. 1 represents a map of land covers identified using the CLC classification system. The 8 selected zones are shown on the map, along with the sites chosen to represent each zone. The pie charts in the figure depict the distribution of these sites across different land covers. Each chart shows the number of sites ($n = 30/\text{zone}$) that fall into different land cover categories.

2.3. EDCs dosage in soil

The detection method employed to quantify these EDCs was adapted from Salvia et al. (2012). This analytical approach enables the simultaneous detection of various emerging pollutants in the complex soil matrix while maintaining a low detection limit. The procedure involves an extraction phase using the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) technique, followed by a purification step utilizing two different cartridges, and finally, analysis using liquid chromatography couple with tandem mass spectrometry (LC-MS/MS).

To adapt this method for a larger sampling campaign, we made several optimizations to reduce the protocol's time without compromising the recovery rate. Additionally, we aimed to achieve better detection and quantification rates. For optimization, we used loamy soil collected from a public garden in Lille, France, spiked with all compounds at 50, 150 and 250 nM (purity >95 %).

For campaign samples, they were extracted from the first 20 cm of soil, homogenized from each location and placed in a dark glass container. Samples were conserved at 4 °C during transportation. They were air dried at ambient temperature after arrival to the laboratory, crushed using a grinder and sieved at 0.63 mm before extraction. They

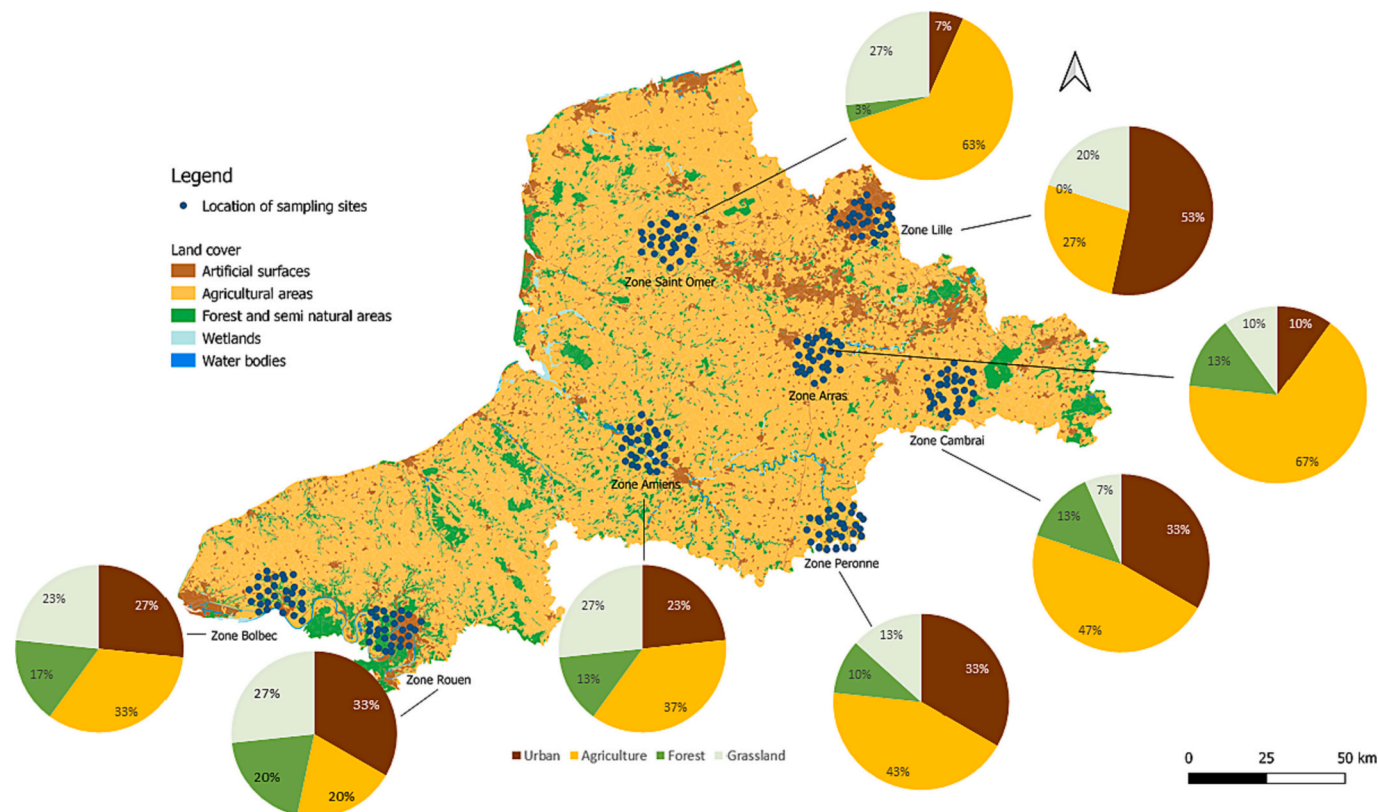


Fig. 1. Map of the study area with the selected sampling sites and their different land covers according to the Corine Land Cover classification. Pie charts represent the distribution of these sites per land cover per zone ($n = 30/\text{zone}$).

were stored for a maximum of 1 week before analysis to minimize the transformation of sex hormones in the soils (Shrestha et al., 2012). Each site was tested in triplicate for accuracy.

The protocol involves an extraction using the QuEChERS method, for which the soil sample was first homogenized and then mixed with magnesium sulfate and sodium acetate buffer. The magnesium sulfate serves to dry the sample, while the sodium acetate buffer maintains the pH of the solution. The mixture is then centrifuged, and a volume of the supernatant was extracted. Instead of extracting 10 mL of the supernatant as per the original method, we extracted 2 mL as Ma et al. (2018) described in their protocol, with a correction factor of 5. The tests between the protocol using 10 mL and the 2 mL revealed a variation between -5.45 % and 20.3 % between the compounds. The time of drying under a nitrogen flow at 40 °C that followed was reduced by 65 %, which is why the protocol of 2 mL extract is used.

The resulting extract was then purified by a Solid Phase Extraction (SPE) method. The purification phase removes any unwanted compounds such as lipids, pigments, and other interfering substances. For this phase, the SAX cartridges (500 mg, 3 mL) and STRATA-X cartridges (200 mg, 3 mL) were used, following the original protocol. The SAX cartridge, with a quaternary ammonium bonded phase, was effective in extracting weak anionic compounds due to its strong anion exchange capacity. The StrataX polymer cartridge was utilized to remove the most hydrophilic compounds. The recovered extract from both cartridges was evaporated to dryness under a gentle stream of nitrogen at 40 °C. Before LC-MS/MS analysis, the dry residue was dissolved in 200 µL of 95/5 H₂O/MeOH and mixed for 20 s.

Analysis was then performed with liquid chromatography (LC) using the UFLC-20XR Shimadzu (Kyoto, Japan). LC was coupled to a 5500 QTrap (Sciex, France) triple quadrupole mass spectrometer, equipped with a turbo electro-spray ion source (turbo-ESI). Both the positive and negative ionization modes were applied, depending on the structural properties of the analytes. The nebulizer gas used was air.

For the analysis of positively ionized compounds (testosterone and progesterone), the Biphenyl Kinetex column (100 mm × 2.1 mm, 2.6 µm) was used. The mobile phases (A) 0.01 % solution of formic acid in MilliQ water (pH = 3.3) and (B) methanol were used. For the analysis of negatively ionized compounds (estrogens and bisphenol A), we used the Zorbax Eclipse XDB C18 column (100 mm × 2.1 mm, 3.5 µm). Mobile phase (A) MilliQ water and (B) 50/50 acetonitrile/methanol were used. To enhance the detection limit of EDCs, 0.05 mM of ammonium fluoride (NH₄F) was added to the mobile phase (A) in negative mode (Gaudl et al., 2016), significantly improving the electrospray ionization, up to 100 times.

The gradient was optimized from 25 min to 17 min in negative mode and from 25 min to 11 min in positive mode without compromising chromatographic separation.

For this method, deuterated compounds were employed as internal standards (IS) for each target compound. These deuterated compounds included 17β-estradiol-2,4,16,16,17-d₅ (for estrogens), naphthol (IS for BPA), Testosterone-2,2,4,6,6-d₅ and progesterone-2,2,4,6,6,17α,21,21,21-d₉, each used at a concentration of 150 nM. To ensure quality control and detect any potential background contamination, blank samples were incorporated into the process. The results from these blank samples indicated the absence of any background contamination.

The limits of detection (LOD) and quantification (LOQ) were determined using a signal-to-noise ratio (S/N) of 3 for LOD and 10 for LOQ, respectively, and were rigorously validated using a loam soil sample collected in Lille, France. The calculated limits of quantification ranged from 0.0043 ng/g for estrone (E1) to 0.43 ng/g for 17β-estradiol (βE2). To assess the recovery of these compounds, soil samples were spiked before and after analysis, with regulation by IS. The recovery rates ranged from 79.49 % to 100.45 %, indicating effective quantification. The use of IS further improved the accuracy of quantification for these compounds. Additional details about the protocol can be found in

Supplementary Materials 2.

2.4. Geographic distribution and data analysis

Maps were created using ArcGIS (10.7.0) and QGIS (3.28.1) software. Land cover data were collected from the Corine Land Cover database.

Statistical analysis was conducted using R (4.1.2) and XLSTAT (2022.4.1). The concentrations of EDCs in soils were reported on a dry weight (dw) basis. Outliers were spotted and eliminated from the statistical analysis of all EDCs compounds and from the maps. The selection of outliers was based on elements with a z-score > 3. Values <LOQ were replaced by the LOQ/2 value for each compound for statistical analysis and geographic representation.

EDCs concentrations in the different sampling areas were compared using the Kruskal-Wallis test (non-parametric test), since the distribution of samples did not follow a normal distribution. The test was used to determine if there were differences in EDCs concentrations between areas as well as between different land covers for each analyte. The level of statistical significance was set at $p < 0.05$. A Spearman correlation test was used to test the correlation between EDCs compounds and a χ^2 test and/or Fisher test were adopted to establish the difference between land covers with respect to the frequency of detection.

To calculate the \sum estrogens, the sum of the concentrations of E1, αE2, βE2, E3 and αEE2 was calculated. To that, the concentration of TES and PRO were added to calculate the \sum hormones and for the \sum EDCs the concentration of BPA was added. This method of calculation was adopted by Yang et al. (2021a) and Liu et al. (2012) among other references to represent the overall concentration of a certain family of elements.

3. Results

3.1. Concentrations of EDCs found in soil in the literature

To establish a baseline for the concentrations of EDCs observed in our current samples, a summary of reported concentrations from previous literature is provided in Table 1. Since there is no predicted no effect concentration of EDCs in soils, these literature values provide valuable reference values.

The reported concentrations of EDCs in soil exhibit considerable variation across different studies. For instance, the reported concentration of E1 ranges from 0.013 to 135.9 ng/g, with the highest concentration found in soil receiving wastewater treatment in the US (Karnjanapiboonwong et al., 2011). The reported concentrations for E2 (including αE2 and βE2) range between 0.51 and 93 ng/g. Fewer studies are reported for E3 ($n = 4$), with concentrations between 0.46 and 6.26 ng/g with one study reporting a mean concentration of 28 ng/g. The concentrations of EE2 in soil are based on three references, two of which show similar range of 2.33 and 2.7 ng/g, while one study reported a high concentration of 86 ng/g in soils treated with biosolids. The levels of PRO range from 1.46 to 31 ng/g, and TES values are between 0.165 and 2.4 ng/g. Notably, BPA has been detected at high concentrations of up to 140,000 ng/g in soils amended with biosolids.

Most of the reviewed studies had small sample sizes ($n \leq 6$), with a few exceptions such as the study from Xu et al. (2021), Isobe et al. (2006) and Zhang et al. (2015b), which included 29, 32 and 20 samples, respectively. One study is based on a large-scale screening of 430 samples (Yang et al., 2021a). Furthermore, it should be noted that studies specifically focusing on hormones did not include analysis of BPA. Therefore, the references for BPA studies differ from those of the hormone studies. In the case of BPA, there are studies with a large number of samples, with one study including up to 210 samples. However, it is important to highlight that the majority of these studies primarily concentrated on agricultural regions and did not consider geographic distribution analysis or diverse site selection. Consequently, the research

Table 1
Concentration of EDCs in soils found in the literature (in ng/g DW) for each compound with the sample location and size.

Compound	Concentration (ng/g dry weight)	Matrix, location and sample size (n)	Reference
Estrone (E1)	0.013 ^b	Manure agricultural application in Northeast China (n = 32)	(Zhang et al., 2015b)
	1.12 ^a	Soil receiving pig manure applications (n = 3)	(Hansen et al., 2011)
	2.74 ^a	Manure agricultural application in Northeast China (n = 32)	(Zhang et al., 2015b)
	9.89 ^a	Agricultural production areas in China (n = 430)	(Yang et al., 2021a)
	10 ^b ± 2	Soil receiving biosolids (n = 3)	(Vigino et al., 2011)
	12 ^b ± 2	Soil from an agriculture watershed that received poultry litter fertilizer (n = 3)	(Tso et al., 2011)
	135.9 ^a	Soil receiving treated effluent from a wastewater treatment plant in the US (n = 4)	(Karnjanapiboonwong et al., 2011)
	0.51 ^b	Manure agricultural application in Northeast China (αE2) (n = 32)	(Zhang et al., 2015b)
	0.675 ^a	Soil with litter application (βE2) (n = 6)	(Finlay-Moore et al., 2000)
	0.9 ^a	Soil receiving pig manure applications (βE2) (n = 3)	(Hansen et al., 2011)
Estradiol (E2)	1.2 ^b	Manure agricultural application in Northeast China (βE2) (n = 32)	(Zhang et al., 2015b)
	3.33 ^a	Soil receiving effluent from a wastewater treatment plant in the US (βE2) (n = 4)	(Karnjanapiboonwong et al., 2011)
	3.46 ^a	Agricultural production areas in China (βE2) (n = 430)	(Yang et al., 2021a)
	5 ^b ± 2.6	Cropland soil in New Castle County, Delaware (βE2) (n = 4)	(Dutta et al., 2012)
	6.5 ^a	Soil receiving pig manure	(Hansen et al., 2011)

Table 1 (continued)

Compound	Concentration (ng/g dry weight)	Matrix, location and sample size (n)	Reference
Estrone (E1)	8 ± 0.9	applications (αE2) (n = 3) Cropland soil in New Castle County, Delaware (αE2) (n = 4)	(Dutta et al., 2012)
	93 ^b ± 12	Soil receiving biosolids (E2) (n = 3)	(Vigino et al., 2011)
	0.46 ^b	Manure agricultural application in Northeast China (n = 32)	(Zhang et al., 2015b)
	5.98 ^a	Soil receiving treated effluent from a wastewater treatment plant in the US (n = 4)	(Karnjanapiboonwong et al., 2011)
	6.26 ^a	Agricultural production areas in China (n = 430)	(Yang et al., 2021a)
	28 ^b ± 9	Soil receiving biosolids (n = 3)	(Vigino et al., 2011)
	2.33 ^a	Agricultural production areas in China (n = 430)	(Yang et al., 2021a)
	2.7 ^a	Soil receiving treated effluent from a wastewater treatment plant in the US (n = 4)	(Karnjanapiboonwong et al., 2011)
	86 ^b ± 12	Soil receiving biosolids (n = 3)	(Vigino et al., 2011)
	0.067 ^b	Manure agricultural application in Northeast China (n = 32)	(Zhang et al., 2015b)
Estradiol (E2)	0.165 ^a	Soil with litter application (n = 6)	(Finlay-Moore et al., 2000)
	0.99 ^a	Agricultural production areas in China (n = 430)	(Yang et al., 2021a)
	2.4 ^a	Soil receiving pig manure applications (n = 3)	(Hansen et al., 2011)
	1.46 ^a	Soil receiving pig manure applications (n = 3)	(Hansen et al., 2011)
Progesterone (PRO)	4.37 ^b	Manure agricultural application in Northeast China (n = 32)	(Zhang et al., 2015b)
	7.0 ± 2.7	Soil sample from vegetable field in Guangxi Province, Southern China (n = 5)	(Liu et al., 2012)

(continued on next page)

Table 1 (continued)

Compound	Concentration (ng/g dry weight)	Matrix, location and sample size (n)	Reference
Bisphenol A (BPA)	12.5 ^a	Agricultural production areas in China (n = 430)	(Yang et al., 2021a)
	31 ^b ± 9	Soil receiving biosolids (n = 3)	(Viglino et al., 2011)
	14.8 ^b ± 3.2	Soil sample irrigated with wastewater from Tula Valley in Mexico City (n = 6)	(Jc et al., 2009)
	166 ^a	Agricultural and urban soil samples from 21 provinces in China (n = 29)	(Xu et al., 2021)
	140 000 ^a	Soil amended with biosolids in Europe (n = 210)	(Staples et al., 2010)

^a Highest concentration reported.

^b Mean concentration reported).

has underrepresented various land uses, such as urban and forest lands.

The significant discrepancies among values reported in the literature are attributed to the selection of the sampled sites, specific soil management practices, and sample size in each study. Some compounds have limited data available since their presence in soils is not as widely recognized. Among the reviewed studies, one comprehensive study conducted in China (Yang et al., 2021a) stands out due to its large number of compounds tested and extensive sampling.

Studies were assessed and selected from the literature to serve as comparison for the findings in this study. The large-scale sampling study conducted in China, involving approximately 430 samples, was chosen as comparative study for E1, β E2, α EE2, E3, TES, and PRO (Yang et al., 2021a). For BPA, the study (Xu et al., 2021), which included 29 sampled sites without focusing on a specific source of contamination, was selected. For α E2, studies were limited, but the selection was based on the study that reported the highest observed concentration (Dutta et al., 2012).

3.2. Concentration of EDCs found in soils of the different study zones

3.2.1. Range of concentrations of EDCs found in soils

The presence of EDCs in the samples varied between the elements. BPA and PRO were detected at all sampling sites, with levels above the LOQ. However, β E2 and E3, values below the LOQ were observed at 82 % and 72 % of the sites, respectively. For the remaining compounds (α EE2, α E2, E1, and TES), the percentage of sites with levels below LOQ were 36 %, 16 %, 5 %, and 12 %, respectively.

Table 2 shows the range of concentrations of EDCs detected in all the samples. The highest concentration of E1 is found in the Cambrai zone at 0.54 ng/g, while the average concentration across the study area is 0.04 ± 0.06 ng/g. α E2 exhibits a high concentration of 3.07 ng/g in Saint-Omer, with an average of 0.21 ± 0.35 ng/g across the study area. β E2 is detected at a maximum concentration of 25.44 ng/g in Bolbec, and an average concentration of 1.06 ± 3.22 ng/g. The average concentration of E3 is 0.12 ± 0.12 ng/g with Rouen showing the highest concentration of 1.20 ng/g. α EE2 is observed at 47.16 ng/g in Rouen, followed by Amiens at 30.80 ng/g. Rouen holds the highest concentration for PRO 6.58 ng/g, and Lille for TES with a highest of 1.02 ng/g. BPA displays a high concentration range compared to other EDCs in this study, reaching

as high as 357.96 ng/g in Rouen. High standard deviations were found among the compounds and particularly for BPA, showing significant variation within sites in the same zone.

The concentrations observed in our study for E1, α E2, E3, TES, and PRO are below the range of values reported in the selected studies in part 3.1. Our findings suggest that these compounds are present at lower levels compared to studies that focused on soils amended with biosolids (Viglino et al., 2011) or soils receiving treated wastewater (Karnjana-piboonwong et al., 2011). However, the levels of β E2, α EE2, and BPA were found to be higher than the comparative studies values. Specifically, the average concentration of α EE2 was found at 1.58 ± 4.68 ng/g and the highest concentration reported is 47.16 ng/g, while Yang et al. reported an average of 0.06 ± 0.17 ng/g and a maximum of 2.33 ng/g. Notably, a study focusing on soils amended with biosolids reported a high concentration of 86 ± 12 ng/g for α EE2, although it only included three samples. Similarly, the mean concentration of β E2 is 1.06 ± 3.22 ng/g, which is higher than the mean concentration of 0.18 ± 0.39 ng/g reported by Yang et al. (2021a) and higher than the concentrations reported in most other studies, except for the aforementioned biosolids study, which reported a concentration of 93 ± 12 ng/g.

The total hormone concentration (\sum hormones), including \sum estrogens, PRO and TES, ranged from 0.64 to 54.58 ng/g, with an average of 4.60 ± 6.98 ng/g. The total concentration of EDCs (\sum EDCs), which includes all compounds, ranged from 3.68 to 364.85 ng/g, with an average of 22.72 ± 35.46 ng/g. The Rouen area has some of the highest concentrations of compounds in the study area, particularly for PRO, E3, α EE2 and BPA.

Compared to the chosen studies' values, our study displayed higher standard deviations for all the elements, indicating significant variation among the sampled sites and notable differences in concentrations. This suggests that the concentrations of EDCs can vary considerably across different sites within our study area.

3.2.2. Spatial distribution of EDCs in the study area

The results obtained make it possible to explore the spatial heterogeneity of EDCs concentrations within and between the delimited sampling areas. Comprehensive map representations have been formulated, delineating concentration profiles of individual EDCs elements, as well as cumulative concentrations of \sum estrogens and \sum hormones.

These cartographic depictions elucidate the dispersion patterns of EDCs concentrations, categorized into five distinct groups, each corresponding to a percentile range within the concentration spectrum. The initial category encompasses the lowest recorded concentration within the study area (min - 25th percentile), followed by the second category encompassing concentrations ranging from the 25th to the 50th percentile. Subsequent categories include the 75th percentile, extending to the 90th percentile for the fourth category, while the fifth category denotes the highest concentration recorded during the study (90th percentile - max value).

For a detailed examination of these spatial distributions, the specific maps are provided in supplementary materials (Supplementary Materials 3). Additionally, Fig. 2 presents a comprehensive overview of the aggregate concentrations of \sum EDCs across all sampled zones.

The map shows a significant variation in the characteristics of each zone, which is determined by the variation in element concentrations (Supplementary materials 3). For example, α E2 shows a significant difference between the zones ($p = 0.000$), with Peronne having the highest average concentration, significantly different than Rouen ($p = 0.000$) and from Saint-Omer ($p = 0.002$), Rouen is, on the other hand, showing the lowest concentrations and significantly different from Lille, Peronne and Arras ($p = 0.001$, $p = 0.000$ and $p = 0.002$ respectively). α EE2 showed a high variation between the zones ($p < 0.0001$), with Peronne showing the lowest concentrations compared to Arras, Rouen and Lille ($p < 0.0001$), which are the highest concentrated zones with α EE2. In terms of E3 concentrations, Cambrai and Arras are significantly different from Saint-Omer ($p = 0.002$, $p = 0.001$ respectively) which

Table 2Range and mean concentration (\pm standard deviation) of analytes in sampled zones and study area in ng/g, compared to literature.

Zones	E1*		α E2**		β E2*		E3*		α EE2*		Σ estrogen*	
	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD
Amiens	<LOQ - 0.18	0.04 \pm 0.04	<LOQ - 0.57	0.15 \pm 0.13	<LOQ - 6.43	0.63 \pm 1.26	<LOQ - 0.40	0.12 \pm 0.09	<LOQ - 30.80	1.83 \pm 5.70	0.45–32.22	2.72 \pm 5.89
Arras	0.01–0.14	0.03 \pm 0.03	0.056–0.97	0.21 \pm 0.20	<LOQ - 21.55	1.77 \pm 4.45	<LOQ - 0.40	0.14 \pm 0.09	<LOQ - 13.28	1.53 \pm 2.87	0.49–35.48	3.66 \pm 7.42
Bolbec	<LOQ - 0.13	0.03 \pm 0.03	<LOQ - 2.36	0.26 \pm 0.50	<LOQ - 25.44	2.06 \pm 5.89	<LOQ - 0.39	0.12 \pm 0.07	<LOQ - 8.51	0.74 \pm 1.69	0.43–35.51	3.18 \pm 7.39
Cambrai	<LOQ - 0.54	0.06 \pm 0.11	<LOQ - 0.99	0.23 \pm 0.24	<LOQ - 14.00	1.11 \pm 3.35	<LOQ - 0.48	0.14 \pm 0.11	<LOQ - 15.89	1.35 \pm 3.11	0.46–30.24	2.86 \pm 6.10
Lille	0.01–0.24	0.04 \pm 0.05	<LOQ - 0.72	0.21 \pm 0.17	<LOQ - 9.64	1.25 \pm 2.58	<LOQ - 0.31	0.10 \pm 0.07	<LOQ - 12.01	1.95 \pm 3.12	0.58–21.96	3.61 \pm 5.10
Peronne	0.007–0.14	0.04 \pm 0.04	<LOQ - 1.41	0.24 \pm 0.27	<LOQ - 13.57	0.74 \pm 2.46	<LOQ - 0.54	0.13 \pm 0.11	<LOQ - 13.40	0.60 \pm 2.42	0.42–28.72	1.75 \pm 5.12
Rouen	<LOQ - 0.14	0.03 \pm 0.03	<LOQ - 2.36	0.20 \pm 0.45	<LOQ - 0.82	0.25 \pm 0.13	<LOQ - 1.20	0.16 \pm 0.24	<LOQ - 47.16	3.20 \pm 9.24	0.47–47.64	3.70 \pm 9.13
Saint Omer	<LOQ - 0.49	0.04 \pm 0.09	<LOQ - 3.07	0.21 \pm 0.56	<LOQ - 6.97	0.71 \pm 1.46	<LOQ - 0.17	0.07 \pm 0.02	<LOQ - 26.62	1.51 \pm 4.91	0.41–26.99	2.54 \pm 5.47
Study area	<LOQ - 0.54	0.04 \pm 0.06	<LOQ - 3.07	0.21 \pm 0.35	<LOQ - 25.44	1.06 \pm 3.22	<LOQ - 1.20	0.12 \pm 0.12	<LOQ - 47.16	1.58 \pm 4.68	0.41–47.64	3.00 \pm 6.52
Literature	<LOQ - 9.89	0.53 \pm 0.91	-	8.00 \pm 0.90	<LOQ - 3.46	0.18 \pm 0.39	<LOQ - 6.26	0.35 \pm 0.96	<LOQ - 2.33	0.06 \pm 0.17	<LOQ - 10.30	1.17 \pm 1.72

Zones	TES*		PRO*		Σ hormones		BPA***		Σ EDCs	
	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD
Amiens	<LOQ - 0.22	0.05 \pm 0.05	0.28–3.98	1.05 \pm 0.88	0.83–33.34	3.79 \pm 6.03	2.01–154.48	14.26 \pm 27.67	5.30–155.31	17.57 \pm 27.10
Arras	<LOQ - 0.22	0.05 \pm 0.04	1.16–4.30	2.09 \pm 0.72	1.74–39.79	5.80 \pm 8.01	0.66–305.38	16.84 \pm 54.58	4.43–307.12	22.64 \pm 54.51
Bolbec	<LOQ - 0.71	0.18 \pm 0.16	0.67–5.78	2.62 \pm 1.58	1.01–39.36	5.80 \pm 7.90	3.10–117.34	19.43 \pm 20.73	4.51–118.35	25.22 \pm 22.78
Cambrai	<LOQ - 0.50	0.09 \pm 0.13	0.27–5.26	1.47 \pm 1.31	0.84–32.12	4.41 \pm 6.50	2.70–26.30	9.30 \pm 4.11	3.85–38.21	13.71 \pm 7.44
Lille	<LOQ - 1.02	0.09 \pm 0.20	0.55–2.51	1.23 \pm 0.54	1.28–24.39	4.92 \pm 5.23	7.31–97.11	27.36 \pm 24.20	10.13–103.00	32.29 \pm 23.98
Peronne	<LOQ - 0.36	0.07 \pm 0.08	0.21–4.63	1.47 \pm 1.16	0.64–30.32	3.23 \pm 5.31	2.50–34.61	11.82 \pm 6.51	3.68–47.78	15.05 \pm 9.00
Rouen	0.02–1.00	0.20 \pm 0.20	0.27–6.58	1.65 \pm 1.39	1.07–54.58	5.56 \pm 10.10	2.84–357.96	35.15 \pm 67.83	10.12–364.85	40.70 \pm 68.00
Saint Omer	<LOQ - 0.33	0.07 \pm 0.07	0.14–2.01	0.66 \pm 0.42	0.67–27.64	3.27 \pm 5.50	3.22–42.83	11.63 \pm 9.30	5.37–44.82	14.90 \pm 10.57
Study area	<LOQ - 1.02	0.10 \pm 0.14	0.14–6.58	1.53 \pm 1.20	0.64–54.58	4.60 \pm 6.98	0.66–357.96	18.13 \pm 34.90	3.68–364.85	22.72 \pm 35.46
Literature	<LOQ - 0.99	0.09 \pm 0.17	<LOQ - 12.50	0.74 \pm 1.25	-	-	<LOQ - 166.00	-	-	-

* Based on the study Yang et al. (2021a, 2021b).

** Based on the study Dutta et al. (2012).

*** Based on the study Xu et al. (2021).

shows no quantifiable concentrations of E3 except in one site. However, for E1 ($p = 0.768$) and β E2 ($p = 0.497$), there are no significant difference between the zones. Consequently, the Σ estrogen shows heterogeneity in the zones, with Lille having the highest estrogen concentrations and Peronne the lowest ($p = 0.0001$).

TES was manifested in Rouen and Bolbec significantly higher ($p < 0.0001$) than the remaining zones. Arras and Bolbec zones have higher mean concentrations than the rest, 2.09 ± 0.72 and 2.62 ± 1.58 ng/g, respectively, particularly compared to Saint-Omer ($p < 0.001$) for PRO concentrations. The Σ hormones concentration indicate Saint-Omer in lower concentrations particularly compared to Arras ($p < 0.0001$), Bolbec, Lille ($p = 0.000$) and Rouen ($p = 0.001$). BPA shows the most heterogenous profiles of the zones, with Arras, Amiens, Cambrai and Saint-Omer representing lower concentrations from Lille, Bolbec and Rouen ($p < 0.0001$), who are on a higher concentration range of BPA. The variability in BPA profiles is reflected in the heterogeneity of Σ EDCs, with the highest concentrations observed in Lille, Rouen and Bolbec, compared to the remaining zones ($p < 0.0001$).

3.2.3. Correlation between EDCs in soils

An interest is held to the possibility of a correlation between the different elements to understand whether there is a connection between these elements or if their presence in soil occurs independently due to different sources. A Spearman correlation test showed that some substances exhibit fair to weak correlations with each other (Supplementary Materials 4). For example, there is a correlation between PRO and E3 ($r = 0.43$), PRO and α EE2 ($r = 0.31$), as well as between PRO and TES, PRO and β E2 ($r = 0.27$), and E1 and α E2 ($r = 0.28$). Correlation between estrogens is either absent or weak. BPA, belonging to a different family of compounds, exhibited a negative correlation with all components. The Σ estrogen is strongly correlated with α EE2 ($r = 0.82$) and moderately correlated with β E2 and α E2 ($r = 0.54$ and $r = 0.47$, respectively). The Σ hormones are primarily correlated with PRO ($r = 0.74$) and moderately correlated with α EE2 ($r = 0.68$). Conversely, Σ EDCs exhibited correlation solely with BPA ($r = 0.86$).

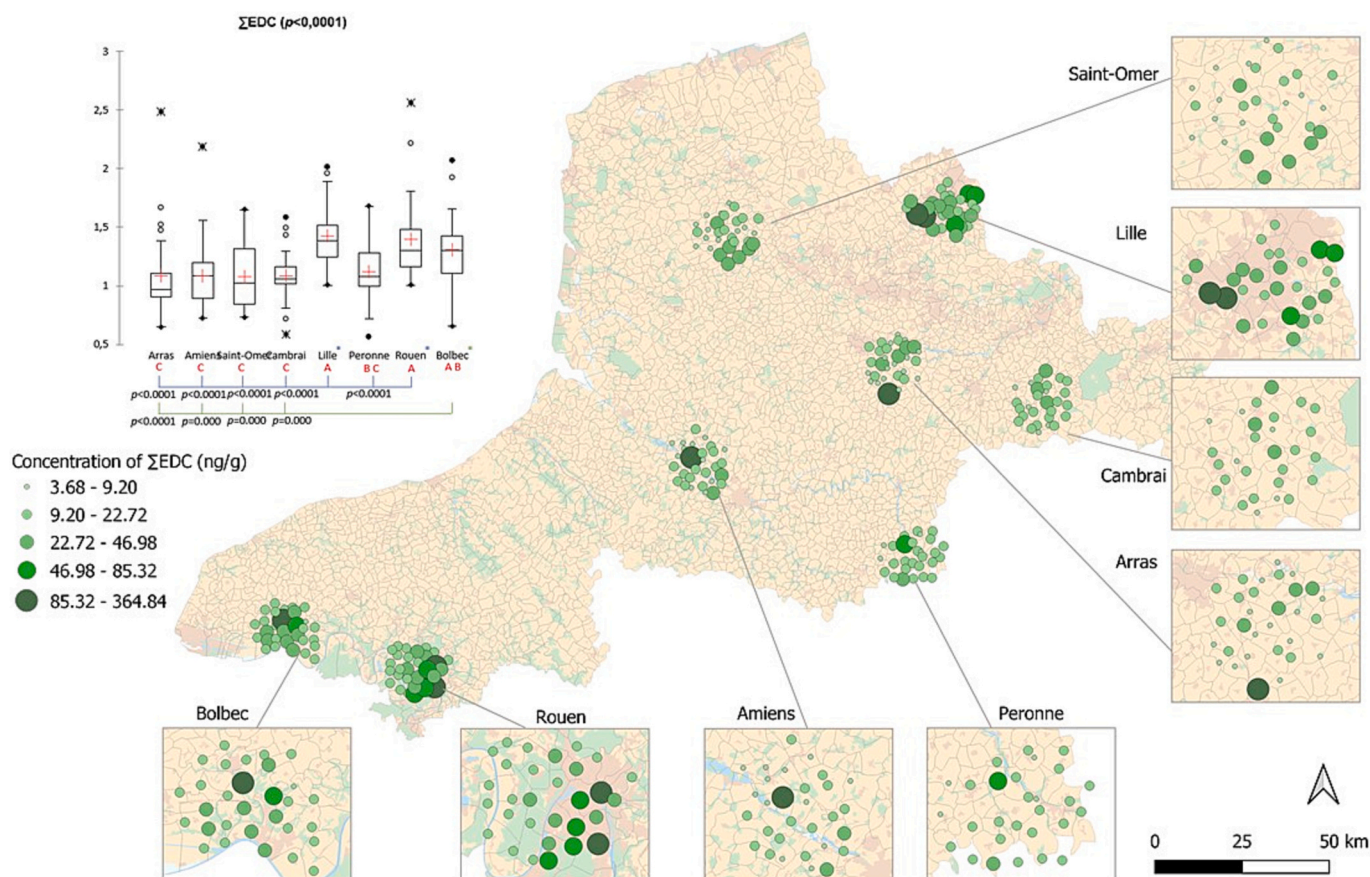


Fig. 2. Spatial distribution of Σ EDCs in sampled zones with zoomed-in views. A Kruskal-Wallis test represents the difference between the zones.

3.3. Analysis of EDCs concentrations in different land covers

In order to comprehend the significant variations in concentrations observed across different locations, a categorization system was employed based on the Corine Land Cover (CLC) descriptions of four primary land covers: agriculture, urban (or artificial areas), forest, and grasslands. The selection of sampling sites was based on a deliberate choice of land covers that accurately represented the entire study area. As a result, 43 % of the selected sites ($n = 101$) were agricultural lands, 27 % ($n = 65$) were urban areas encompassing major cities such as Lille and Rouen, 19 % ($n = 46$) were grasslands, and 11 % ($n = 27$) were forests and semi-natural lands. Specifically, two geographic zones, Lille and Rouen, were targeting the main urban agglomerations of the study area with 53 % and 33 % of their selected sites were collected from urban or artificial soils, respectively. Zones with predominance of agricultural sites were Arras, Saint-Omer and Cambrai with 67 %, 63 % and 47 % of sites in agricultural spots respectively, with a focus on sites that receive amendments of biosolids. Forests are represented mostly in Rouen and Bolbec with 20 and 17 % of sites respectively. The remaining zones have an average of 13 % of forests except for Lille who does not have forests in its territory. Grasslands are represented in 27 % of sites of Amiens, Saint-Omer and Rouen.

The detection frequency of the different compounds was variable between land covers. While PRO and BPA were found at almost all sites and land covers, the frequency of EDCs detection varied across different land covers.

β E2 and E3 exhibit the lowest detection rates among the 240 surveyed sites, registering a detectability of 17.15 % for both compounds (supplementary materials 5). However, their detection prevalence varies significantly across different land covers. Specifically, in forested areas, E3 and β E2 demonstrate higher detectability compared to other land

cover types, accounting for 51.85 % and 29.63 % detectability in forested lands, respectively. Notably, α EE2 also exhibits substantially elevated detectability in forested areas, with 88.89 % of sites demonstrating detectability. Conversely, BPA, PRO, and E1 display the highest detectability, with minimal variation observed across different land covers, ranging from no difference to very low differences (Fig. 3).

There is an overall tendency for concentrations to be higher in forest areas, average in urban and grassland areas, and lower in agricultural areas according to a Kruskal-Wallis test. Forests are significantly more contaminated ($p < 0.001$) for α EE2, E3 and PRO than remaining land covers. The agricultural environment is significantly less contaminated for PRO and TES soils than other land covers with a significant difference $p < 0.0001$ with forest, respectively. However, there are no significant differences for α E2, β E2, E1 and BPA (Fig. 4).

The same trends were found for the sum indicators. The concentration of estrogens, as indicated by the Σ estrogen parameter, is significantly higher in forested areas compared to other land covers ($p < 0.0001$). This trend is also observed for the Σ hormones parameter, with lower concentrations found in agricultural lands ($p < 0.0001$). Conversely, agricultural lands have lower concentrations of EDCs compared to urban and forested lands ($p = 0.000$) and forest lands are significantly different ($p < 0.000$) from agricultural and grasslands.

It is relevant to note that these values are studied after elimination of outliers. From the deleted outliers, 48 % of which were sampled in forest and semi-natural lands. The most extreme concentration that was recorded in this study for each of the 7 compounds was located in a forest land.

In addition to land-use assessment, a deliberate selection was made to include sites with distinct sources of EDCs. These included agricultural areas with sludge spreading, areas within industrial zones, sites subject to intense grazing and agriculture, and sites listed in the BASIAS

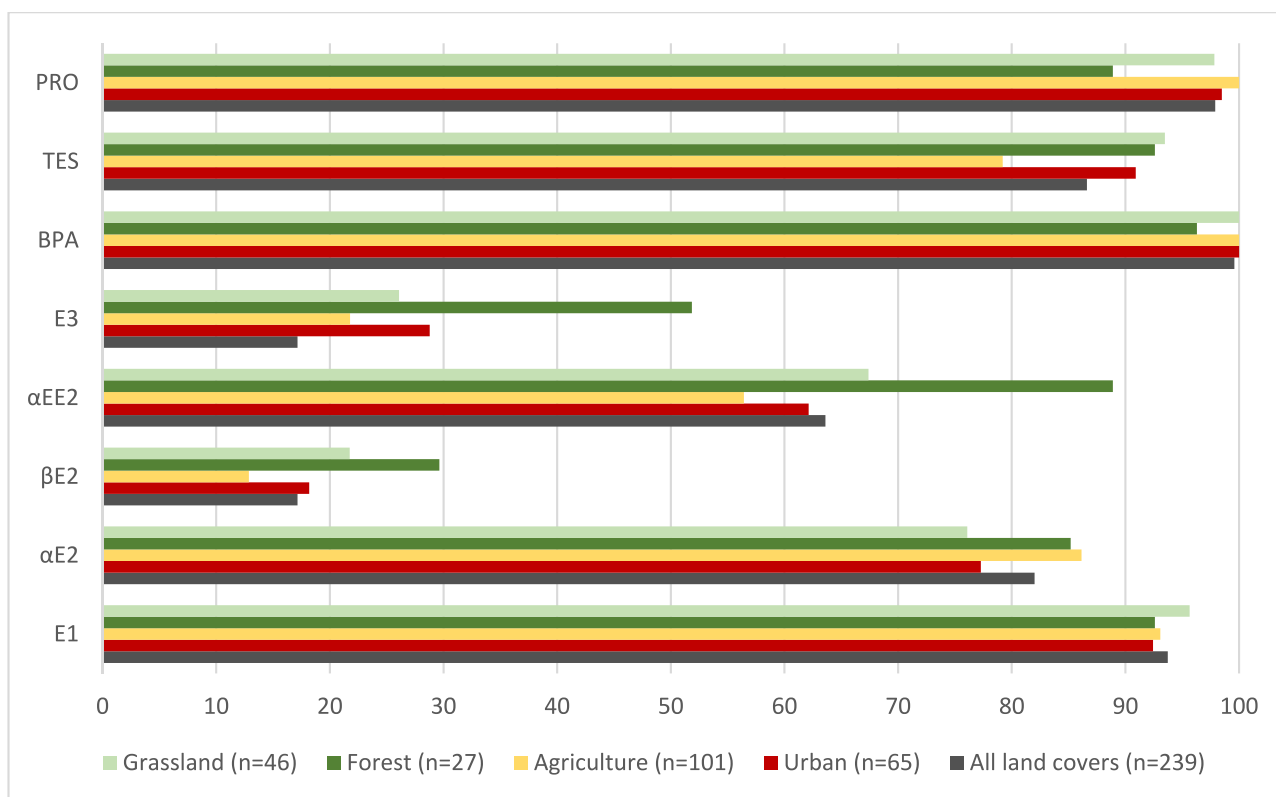


Fig. 3. Detection frequency (%) of EDCs found in the soil samples.

database associated with agricultural landfills or former industrial sites linked to the food industry. The survey revealed significant variations in EDC concentrations between the selected sites. In particular, farms and grazing land had higher concentrations of testosterone and progesterone than agricultural land with sludge application ($p = 0.0024$ and $p = 0.00065$, respectively). In addition, industrial sites had significantly higher BPA concentrations than other sources ($p = 0.000$). In the case of estrogens, no significant differences were observed between the specific sources initially considered. However, when the analysis was extended to include forest land and urban areas, all estrogens, with the exception of E1 and αE2, showed significantly higher concentrations in forest land. Among them, βE2, EE2 and E3 showed notable concentrations in forest land ($p = 0.034$, $p < 0.0001$ and $p = 0.003$, respectively). These results are detailed in Supplementary materials 6.

4. Discussion

This study aimed to evaluate eight EDCs concentrations in 240 French soils samples, including various types of land covers and landscapes.

4.1. Concentrations reported in soils

Considered as emerging pollutants in the environment, EDCs are newly identified pollutants and not yet monitored in soils (Rodríguez Eugenio et al., 2018). While the concern over these emerging pollutants in soils was highlighted in a report published by the FAO in 2018, there has been a lack of significant international or national alarm regarding this issue. Specifically, substances such as androgens, estrogens, and progestins, which are nonvolatile and slightly hydrophobic based on their physicochemical properties (Liu et al., 2012), have the ability to bind to sediments and soils and can potentially leach into underground water and surface waters (Bai, 2020).

Efforts to quantify and detect these EDCs in soils have been hindered

by limited sample sizes ($3 < n < 6$) as part of the application of experimental protocols. Additionally, the focus has primarily been on specific pollution sources, such as the use of biosolids in agricultural soils. Biosolids, which are nutrient-rich organic materials from wastewater treatment, are known to contain high concentrations of hormones (Bevacqua et al., 2011) and BPA (Zhang et al., 2015a) when added to soil. One study examined 32 samples of agricultural soil with a history of heavy manure application (Zhang et al., 2015b), while another extensive screening for these EDCs in agricultural lands in China involved 430 soil samples (Yang et al., 2021a).

The concentrations of EDCs reported in various studies, as summarized in Table 1, exhibit considerable variation. Specifically, the concentration of E1 is ranged between 0.013 and 12 ng/g as mean concentrations found in different studies, as for EE2 for example, the mean concentration of one study is reported to be 86 ng/g while the highest reported concentration in another study was 2.33 ng/g. This substantial variability in concentrations can be attributed to the influence of soil parameters, different sources of estrogens, or variations in analytical quality. Our study's findings fall within the higher range of concentrations for βE2, BPA and EE2, but within the very low range for E1, αE2 and E3 reported in the literature. Similarly, for TES and PRO, the variance between the highest and lowest reported concentrations in the literature is considerable. The highest concentrations of TES and PRO reported in our study align with the ranges observed in the literature, while their average concentrations tend to be towards the lower end.

The low concentrations reported in our study suggest a minimal influence of sporadic sources of EDCs in the environment. These findings provide valuable insights into the distribution and variability of EDCs concentrations in soils, emphasizing the importance of considering various factors that may influence their presence in the environment.

4.2. Geographic variability

Variability of intra-zone and inter-zones was assessed to determine

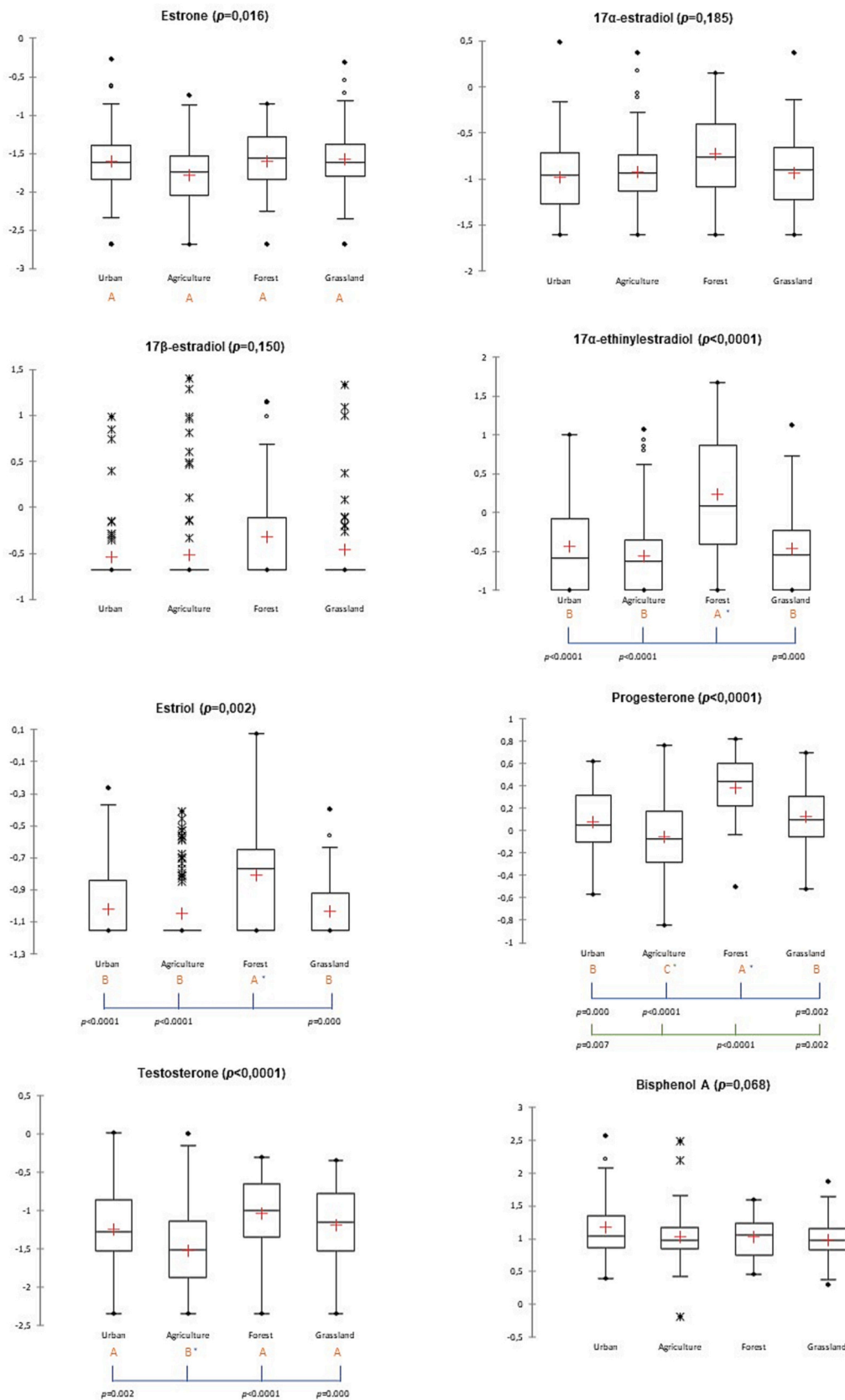


Fig. 4. Comparison of EDCs in different land covers using Kruskal-Wallis test: Box plots and statistical differences. (Note: Asterisks (*) indicate significant differences between zones. The line below each asterisk indicates the zone(s) with significant differences, and the corresponding p -value is shown beneath the line. If multiple zones share the same p -value, a single value is displayed for the entire area. If two occupations exhibit significant differences, two lines are represented in different colors.)

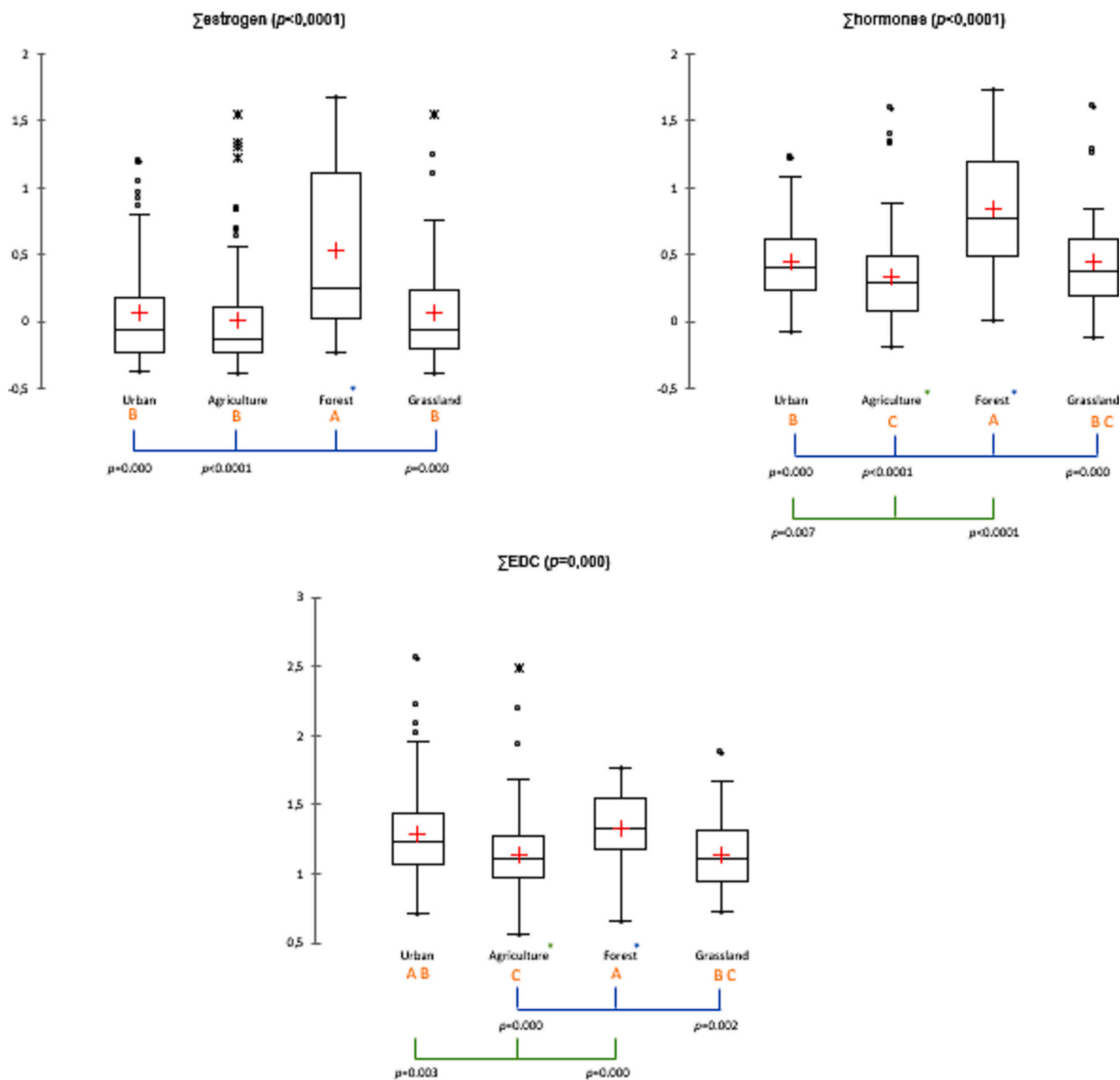


Fig. 4. (continued).

the distribution of these EDCs in the study area and assess the occurrence of the compounds depending on geographic distribution. The detection rates of these EDCs varied among the sites, but at least 3 compounds were detected in each site.

Among the compounds studied, $\beta\text{E}2$ and $\text{E}3$ had the lowest detection frequency, being detected in only 17 % of the sites and BPA and PRO detected in almost all sites. The highest concentration of $\beta\text{E}2$, at 25.44 ng/g, was found in Bolbec and the highest of $\text{E}3$ at 1.20 ng/g in Rouen. Rouen also holds the highest concentrations of BPA, $\alpha\text{EE}2$ and PRO. Furthermore, $\alpha\text{EE}2$ and TES were detected in 64 % and 87 % of the sites, respectively. The highest concentrations detected for $\alpha\text{EE}2$ and TES ranged from 8.51 to 47.16 ng/g and 0.22 to 1.02 ng/g, respectively. These values for $\alpha\text{EE}2$ are higher than the concentrations reported in previous literature. The highest concentrations of $\beta\text{E}2$ ranged from 0.82 to 25.44 ng/g, while the highest concentration in the reference is set at

3.46 ng/g.

BPA exhibited significant variation between zones, with the highest concentrations of 26.30 ng/g in some zones and 357.96 ng/g in others. The average BPA concentration in the study area was 18.20 ± 35.03 ng/g, highlighting a substantial difference between sites and zones. This variation was also reflected in ΣEDCs in the study area, which exhibited a high standard deviation. There was significant deviation from the mean concentrations in most zones, indicating substantial variation in pollutant levels among sites within the same zone visible on the map showing the ΣEDCs .

This study found that, overall, the concentration of the EDCs is higher in forest lands compared to agricultural lands ($p < 0.0001$), highly influenced by the high concentrations of $\alpha\text{EE}2$ and $\text{E}3$ in forest and semi-natural lands. EDCs in the study area showed non-uniform distribution and varied between zones due to different sources, land

cover, and land management practices. Each EDCs compound had a specific distribution pattern and was not uniformly present across all sites. The occurrence and concentration of EDCs depended on their respective sources and environmental factors.

A weak correlation was observed among the different EDCs compounds, with the strongest correlation found between PRO and E3, as well as between PRO and α EE2. This correlation suggests that the origins of these compounds are not uniform and may originate from diverse sources within the soils. In the study conducted by Yang et al. (2021a, 2021b), which focused on agricultural lands, a more pronounced correlation between the compounds was observed. The same observation was made of inter-transformation among steroid estrogens (Yang et al., 2021b). The variety of land covers in our study area may lead to a diverse array of sources for these EDCs, while in cases with the same land cover, the sources may be more interconnected.

α EE2 showed a high correlation with \sum estrogen and \sum hormones, indicating its influence on the overall values of these parameters. Additionally, there was a strong correlation of 0.86 between \sum EDCs and BPA.

The correlation pattern was reflected in the higher representation of Lille and Rouen zones in the \sum EDCs, which are more urban (Corrales et al., 2015) and characterized by higher BPA concentrations. Although Lille exhibited a wider range of α EE2 and consequently higher \sum estrogen values, it did not have the highest concentrations of other EDCs compounds. It is worth noting that Saint-Omer consistently showed lower concentrations of all eight EDCs, despite having the highest percentage of agricultural lands, which are the main source of these compounds in soils.

4.3. Land use influence on contamination distribution

The presence of EDCs varied depending on the land cover of the site, including urban, agricultural, grasslands, and forest or semi-natural areas. Forest lands had the highest detection rate of EDCs, with notable concentrations of PRO, E3 and α EE2. Agricultural lands had the lowest frequency of EDCs detection, while urban and grassland sites exhibited concentrations closer to the median for EDCs. Currently, there is limited information on how land use affects the detection and contamination levels of EDCs. These compounds primarily enter the environment through agricultural practices, wastewater treatment, and landfills. Natural hormones excreted by humans and animals have a half-life in soil ranging from 1 to 10 days, although this varies across studies (Ying and Kookana, 2005; Bai, 2020; Lee et al., 2007). They degrade rapidly under high temperature and aerobic conditions (Moody et al., 2023). It has been found that EE2 is more resistant to degradation in the environment when compared to natural estrogens, and therefore may pose a more significant environmental risk (Adeel et al., 2017). The frequent detection of EDCs at high concentrations in soils, despite their short half-life, is perplexing. Furthermore, the presence of these compounds in forest soils, where no known contamination sources exist, raises additional questions. Forest soils, characterized by high organic matter, water-holding capacity, (Osman, 2013), low soil aeration, low temperatures (Boyle, 2005) and low pH levels (Li et al., 2013), may contribute to the preservation of these EDCs (Deksissa, 2009; Neale et al., 2009).

This study revealed the presence of elevated concentrations of EE2, PRO and E3 in forest soils. These compounds are predominantly linked to agricultural practices as known sources in soil. However, no significant differences in estrogen concentrations were observed between their respective sources. Previous research on EDCs in soils has primarily focused on agricultural lands where biosolids or manure amendments are applied. Consequently, there has been no established link between woodlands and the presence of these compounds in soils. Considering the current knowledge about the sources of these molecules in soils, the origins may be attributed to runoff from agricultural lands, as up to 86 % of hormones have been detected in the runoff of agricultural areas with

manure treatment (Biswas et al., 2017). Additionally, the disposal of sewage sludge has been identified as a contributor to EDCs in soils (Bolesta et al., 2022), particularly given that the selected forest lands had previous industrial service based on BASIAS database records. Furthermore, animal and industrial waste also represent potential sources of EDCs in soils (Li, 2014). However, the lack of historical and management practice information for these forest lands makes it challenging to ascertain the accuracy of these hypotheses.

4.4. Scopes of the study

There are several limitations to our study that must be acknowledged in order to define its scope. The most important is the lack of established reference values for the EDCs of interest in soil. Although predicted no-effect concentrations (PNECs) are available for these EDCs in water, with values of 0.4, 3.6, 60, 0.35, and 240 ng/L for β E2, E1, E3, EE2, and BPA, respectively (Caldwell et al., 2012), PNEC values have yet to be established for these emerging pollutants in soil. The PNEC indicates a limit concentration to its effect on the ecosystem. Since these compounds, especially the synthetic ones, are not naturally found in the soils, any concentration found in the soils can be considered a contamination. Therefore, a reference of PNEC should be an indication of the concentration's effect on the ecosystem. In the absence of established reference values, our study represents a first step towards compiling soil contamination data for international comparison, considering the land use. This first step is crucial to the development of a standardization strategy that will enable conclusions to be drawn concerning environmental pollution or human toxicology.

Another limitation was the representation of the sum of families. The sum of each group of compounds provides an estimate of the total pollution at a given site. However, this sum may be strongly influenced by one or more compounds with high concentrations, which may distort the results. For example, in the case of \sum estrogens, it was highly correlated to α EE2, which had a higher concentration than the other estrogens, giving it a tendency to dominate the sum of estrogens. Similarly, BPA significantly affected the range and mean of the \sum EDCs calculation, which is shown by the high correlation between them ($r = 0.86$). Therefore, relying solely on this calculation for inter-site comparisons may result in variations based on one or two dominant compounds. To address this challenge, different indicators can be used, such as the Mean Impregnation Ratio (MIR) (Ocelli et al., 2016) or the use of z-score normalization. The MIR is a composite index used to calculate total contamination that depends on a background reference for each element or a toxicity level. However, in this study, such references are not available. On the other hand, the z-score normalization allows meaningful comparisons between data points from different data sets with different units of measurement and scales. However, statistical comparisons between z-scores are not applicable. A complete comparison and interpretation of soil contamination by a complex mixture of multi-EDCs therefore requires a careful preliminary assessment of possible indicators and, once calculated, a nuanced examination considering the limitations of the selected indicator.

5. Conclusion

This study significantly advances our understanding of EDCs, an emerging group of pollutants with limited environmental monitoring, especially in soils. Our main objective was to conduct a large-scale campaign, enriching the data on EDCs in soils using an optimized and sensitive experimental protocol. The results obtained from analyzing 240 soil samples across different environments in northern France revealed widespread presence of EDCs, particularly synthetic estrogens at higher concentrations. Surprisingly, forest lands exhibited higher EDCs occurrence compared to agricultural lands, challenging existing hypotheses based on known sources. This intriguing finding calls for further investigation into the sources and persistence of these

compounds in the environment. The study highlights the complex nature of EDCs distribution and emphasizes the need for comprehensive analysis considering multiple sources. Future research must assess potential impacts on ecosystems and human health, establish concentration thresholds of concern, and develop mitigation strategies. Our findings provide a valuable reference for future soil studies and underscore the urgency of continued research to address EDCs' environmental implications.

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CRediT authorship contribution statement

L.M. Wakim: Conceptualization, Data curation, Formal analysis, Visualization, Writing – original draft. **F. Ocelli:** Project administration, Supervision, Writing – review & editing. **M. Paumelle:** Writing – review & editing. **D. Brousriche:** Writing – review & editing. **L. Bouhadj:** Writing – review & editing. **D. Cuny:** Project administration, Supervision, Writing – review & editing. **A. Descat:** Formal analysis, Methodology, Writing – review & editing. **C. Lanier:** Writing – review & editing. **A. Deram:** Conceptualization, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author used Chat-openai to improve readability and language. After using this tool, the author reviewed and edited the content as needed and take full responsibility for the content of the publication.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.169617>.

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