Mixtures of sediment chemical contaminants at freshwater sampling sites across Europe with different contaminant burdens

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Highlights

- A gradient of pollutant mixtures is apparent across sites characterised by Principal Component Analysis.
- Legacy contaminants present in all survey regions at elevated concentrations.
- Watch list contaminants ubiquitous but at generally low concentrations.
- Narrow analytical suites will not accurately characterise complex nature of contaminant mixtures in sediments.
- Sediment size and contaminant relationship; fine material had high chemical loads.

Abstract

Extended chemical analyses of fluvial sediments were undertaken to establish the key pollutant pressures and mixtures present across nine European Union inland waterways. A wide range of chemical components and physical parameters were investigated including substances from the EU Priority List and Watch List. The data set was examined for key indicator compounds, however it was found that a wide range of pollution pressures were present in the different sediments including organic hydrocarbons, metal(loid)s, nutrients, polycyclic aromatic hydrocarbon (PAH),

polychlorinated biphenyl (PCB) compounds, perfluoroalkyl and polyfluoroalkyl substances and pesticides, some of which exceeded regulatory guidance at different sampling points. The presence of such a wide range of compounds underpins the complex chemical composition of sediments that have acted as sinks for many decades absorbing contaminants from urban, industrial and agricultural sources. This dataset has been used to describe average overall toxicity of the sediments sampled, a calculation which was based on key components identified by Principal Component Analysis (PCA) and for those that had existing freshwater sediment regulatory values. A total of 33 components were used including PCBs, PAHs, metal(iod)s and pesticides. This analysis reflected the contamination of each site, with most indicating some level of toxicity during the sampling period. Watch List chemicals triclosan (TCS) and diclofenac (DIC) were also investigated; levels were relatively low, typically 10 -100's ng L^{-1}, however they were present at all sampling sites. The dataset is available as a resource for future chemical, and toxicological, sediment analysis comparisons.

Keywords: emerging contaminants, fresh-water sediment monitoring, chemical mixtures, forever chemicals.

1. Introduction

Sediments are an important, dynamic part of the aquatic ecosystem providing habitat for benthic organisms[1] but also acting as a significant sink with the potential to accumulate and store a large range of contaminants.[2] Following significant improvements in surface water quality it is now expected that sediments could act as a large source of secondary contamination for organisms present within the wider aquatic ecosystem.[2-4] Despite this recognised importance there are only limited regulatory guidelines for fresh water sediments.[5] Further to this most studies of potential toxicity are targeted to small groups or classifications of compounds such as metals or polyaromatic

hydrocarbons. Such studies fail to represent the full range of chemical mixtures present in a sediment and thus their potential combined toxicity. To address this there is great need for comprehensive monitoring to assess broader matrix and potential cocktail of pollutant pressures present.[6] [7]

Since the introduction of the tighter regulations requiring more extensive monitoring, including directives such as the EU Water Framework, Priority List and Nitrate Directives, driving improvements in waste water treatment, waterways have become cleaner.[8] Regulation has driven technologies to both clean and monitor waterways for many contaminants. However, sediments still act as sinks for contaminants, potentially released decades before these intentions, storing compounds for many years. When disturbed (e.g. during dredging or flood events), a large cocktail of contaminants can then be remobilised into the water column, leading to sediments being considered as a potential pollution source and, as such, requiring careful characterisation and management.[2, 3, 9] Such monitoring may become a vital part of achieving the 'good ecological status' which is set out by the EU Water Framework Directive (WFD, 2000/60/EC), now transposed via the Water Environment [England and Wales] Regulations 2017.[10]

Furthermore, there is growing evidence that many of the inland waterways in the European Union are impacted by Watch List chemicals (WLCs) that are not currently regulated under the Water Framework Directive.[11] These chemicals include the known Priority List and WLCs including endocrine disruptors such as oestradiol (E2), and the contraceptive pill (ethinyloestradiol), and other pharmaceutical drugs and antibacterial agents such as diclofenac (DIC) and triclosan (TCS), which have all been shown to be harmful to wildlife.[12, 13] Emerging contaminants, including TCS and DIC, are of concern due to endocrine disrupting properties.[14] Often these organic molecules are sparingly soluble in water but do accumulate and persist within the sediment.[15] Such chemicals are introduced into waterways as a result of anthropogenic activities that introduce both point and

non-point contamination sources.[11] Yi *et al.* reported how anthropogenic activities are impacting waterways as common sources of antibiotics in water and soil.[16] Regardless of the source, they accumulate in the sediments over long time scales and are rarely monitored alongside other chemical contaminants. This is reflected in the lack of well-developed guidance for sediments in comparison to the water column. The majority of published literature to date on detailed studies regarding chemical contaminant profiles (priority list and emerging compounds) are patchy, based on targeted spot sampling or modelling with limited detailed sampling that gives a deep understanding of the potential toxicity of sediments. One of the few examples of a comprehensive study was undertaken by Whelan *et al.* who's review of water quality in the current day in comparison to industrial revolution times concluded that over time water quality pressures have changed related to anthropogenic changes. [17] This work highlighted the need for detailed and comprehensive analysis of the fresh water environment for full and complete characterisation.

The aim of this work was to characterise nine sites across the Northern EU region with a range of land use and industrial pressures in such detail as to enable regulators and water managers to make better decisions with regard to sediment management, removal and disposal, by characterising the chemical composition of the sediments and thereby reducing economic costs and impact of these chemicals on the environment. Presented here are the results from a detailed, harmonised sediment sampling programme across freshwater environments, of differing contaminant pressure profiles, within North-western Europe.

2. Methods

2.1 Sampling sites

Nine sample from across the North Sea region where sampled (Figure 1) these represented a range of geographic settings (e.g. hydrogeographic, land use) current and historical pollution pressures in

the North East Atlantic region (Table I). At each sampled region, the three sites were chosen in such a way, that one should be exposed to the effluents of a WWTP in order to study the impact from the use of personal products and pharmaceuticals as remains in WWTP emissions, one should be situated upstream of the WWTP, and the third one was chosen to reflect a contamination gradient.

Table 1: Locations and physical descriptions of each sampling site, Elbe Region, Scheldt River Basin District (Scheldt RBD), and Humber catchment.

	Scheldt RBD			**Elbe region**			**Humber catchment**		
Area	36 500 km^2			150 000 km^2			26 100 km^2		
Popn.	> 10 million			23 million			11 million		
	BE1	BE2	BE3	DE1	DE2	DE3	UK1	UK2	UK3
Name	Scheldt upstr. WWTP	Scheldt downstr. WWTP	Zenne	Stover Strand	Köhlbrand	Wedel	Aire upstr. WWTP	Aire downstr. WWTP	Pockling-ton Canal
Coordinates	50.858406°	50.869987°	50.960414°	53.425837°	53.527397°	53.567499°	53.766464°	53.766423°	53.897416°
	3.626400°	3.628108°	4.455655°	10.293371°	9.937781°	9.676756°	1.480363°	1.473260°	0.806279°
Water depth (m)	4.0-8.0	4.0-8.0	~ 2.0	2.0-2.8	12	16.0-16.8	0.2-1.2	0.5-1.2	0.4-1.8

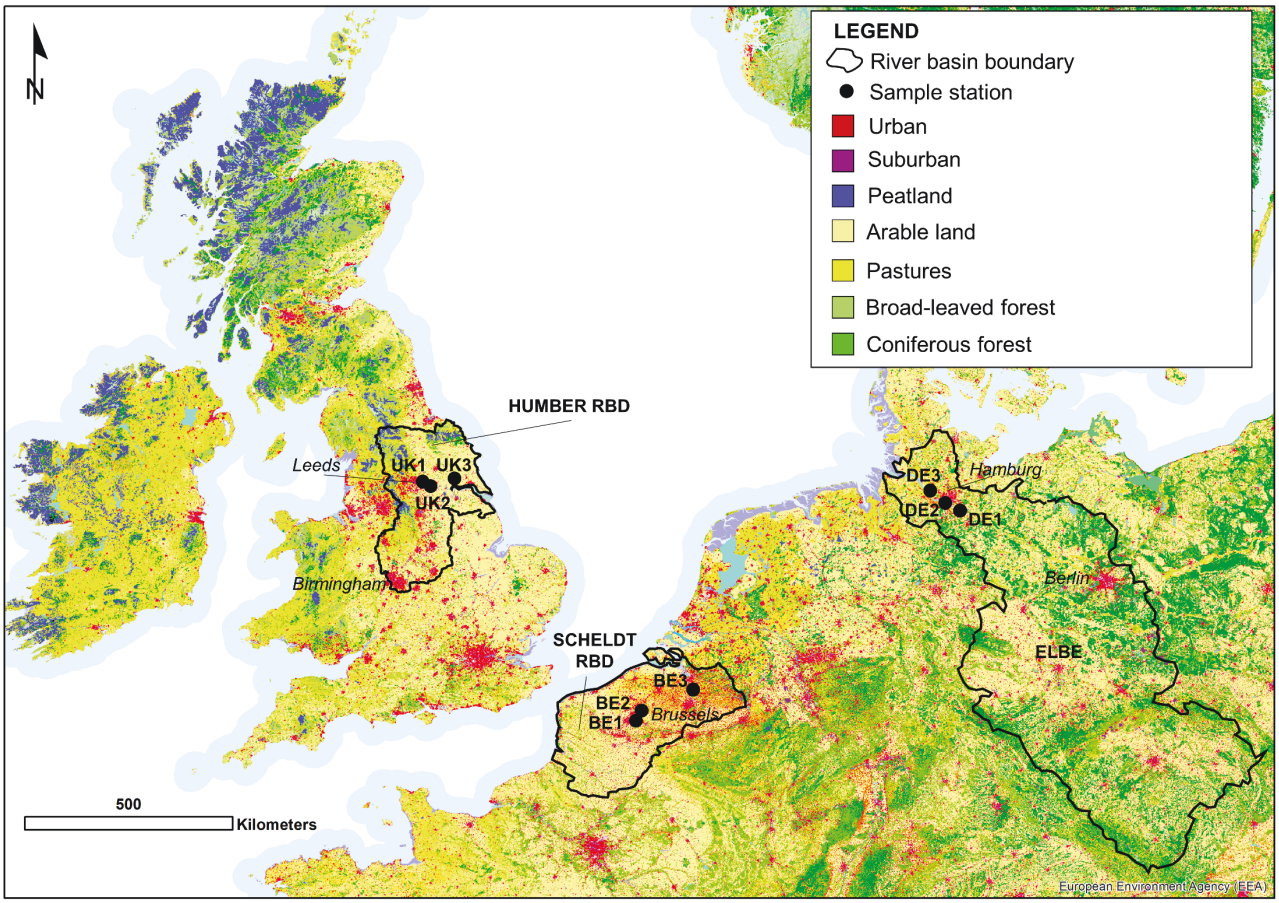

Fig. 1: Sampling sites across the North Sea region in the Elbe catchment, Scheldt River Basin District (RBD) and Humber RBD. Background land use data from CORINE land cover dataset (EEA, 2018).[19]

2.2 Sampling methods

Six sediment sampling campaigns were undertaken in autumn 2017, spring, summer and autumn 2018, spring and summer 2019. At each site and depending on the size of the grab sampler, 15-40 samples were taken within a designated sample reach of 100 m, pooled and homogenised with mechanical stirring for at least 6 minutes. Following this samples were divided and stored in sealed containers at 4 – 8 ^{O}C before analysis. For nutrient, perfluoroalkyl and polyfluoroalkyl substances (PFAS) and metal analysis samples were stored in high density polyethylene plastic containers, oils, dioxins and WLCs glass containers were used, for remaining organic substances metal containers

were used. For long term storage samples were freeze dried and then stored at -20 ^{O}C. Full details of the sampling procedure can be found in the supplementary sections 1 and 2.

Chemical analysis methods

A range of compounds were considered for chemical analysis, this included 53 hydrocarbons, 26 metals and metalloids, 15 dioxins and furans, 16 EPA PAHs, 7 PCBs, 8 organotin compounds, 10 pesticides, 15 per- and poly-fluoric compounds and emerging contaminants, TCS, DIC and E2. These where analysed using gas chromatography (GC) for hydrocarbons, organotin compounds, gas chromatography mass spectrometry (GC/MS) for PAHs, PCBs, dioxins, furans and pesticides , liquid chromatography spectrometry (LC/MS) for perfluoric compounds and watchlist chemicals, inductivity couple plasma mass spectrometry (ICP-MS) and inductively couple plasma optical Emission spectroscopy (ICP-OES) for metals and metalloids and colourimetry for nutrient analysis. A full list of all parameters quantified can be found in the Appendices/Supplemental Information section. Acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) measurements where used for SEM-AVS ratio, organic matter content, grain size distribution and nutrient levels (available phosphates, nitrate, nitrite, exchangeable ammonium) were also measured. Comparative analysis was also carried out as detailed in the supplementary section S2.

2.3 Statistical methods

Statistical analysis, including minimum, maximum and mean average values, were calculated for the full data set including all chemical and physical parameters. From this box plots were generated with inclusive medium values, showing median value, interquartile range (IQR), mean average value (marked as an x) and outlier values. The box plots cover the full data set, n = 9 sampling sites x 6 sampling rounds, 54 data values for each measured parameter.

Principal component analysis was carried out to provide insight into the stressors for each region, and allow for a comparison and characterization of sites. It was conducted using the program MVSP

with 71 variables (chemical analytes and grain size distribution) and 53 cases. The list of variables is included in the supplementary material. From the range of analytes measured in this project, those variables with a high number of non-detects (o'p'-DDX, bor, other organitin compounds than butyl tins) were omitted. Non-detects were replaced by 0.5 times the limit of detection, following Hites, 2019.[20] The data was $\log_{10}$ transformed, with tolerance of eigenanalysis set at 1^{-7}, standardized and granulometrically normalized to the fraction <20 µm (metals) and <63 µm (organic substances), respectively.

Of the 54 cases that represent the samples from three countries, three sites, and six sampling surveys, one sample, UK5_2, was excluded from the analysis because it had almost no grain size fraction smaller than 63 µm (<0.05 %), rendering the granulometric normalization ineffective for this sample.

Sediment quality guideline quotients (SQGQ) were calculated for each site taking into account the exceedance of each component compared to suggested guideline values (PEL values) and reported as an average of all six sampling rounds, the specific calculation is shown by equation 1. A total of 31 compounds were considered, including metals, individual PAHs, PCBs and pesticides. These contaminants were chosen for further calculations based on numerical effect-based sediment quality guidelines being available. These are empirical derived guidelines from databases of sediment chemistry and observed biological effects. Among the various SQG available, the "probably effect levels" (PEL), derived by de Deckere et al., are used.[21] By comparing environmental concentrations with PEL values, any exceedance indicate that toxic effects are likely. TEL values, which will be addressed later on, reflect a "threshold effect level". Concentrations below a TEL are unlikely to occur. Box plots were generated for each sampling site, n = 6.

$$SQGQ = \frac{\sum\left(\frac{average\ contaminant\ concemtration}{SQG}\right)}{n} \qquad \textit{Equation 1}$$

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3. Results

Key results are presented here showing and overview of the contamination presence across the 9 sites shown in figures 2 to 4, table II and SI section 3 to 5.

3.1 Key contamination pressures across the nine sites

A total of 54 homogenised sediment samples were taken across the sampling period (summer 2017 to spring 2019) over the 9 sampling sites. Each was analysed for a wide range of chemical contaminants and physical parameters including metals, hydrocarbons, PAHs, PCBs, nutrients, pesticides, emerging contaminants (TCS and DIC), perfluoric compounds, pH, redox, organic matter and grain size. Contaminant concentration varied across the region with most sites showing concerning levels of at least one of the contaminants studied, results shown in figure 2.

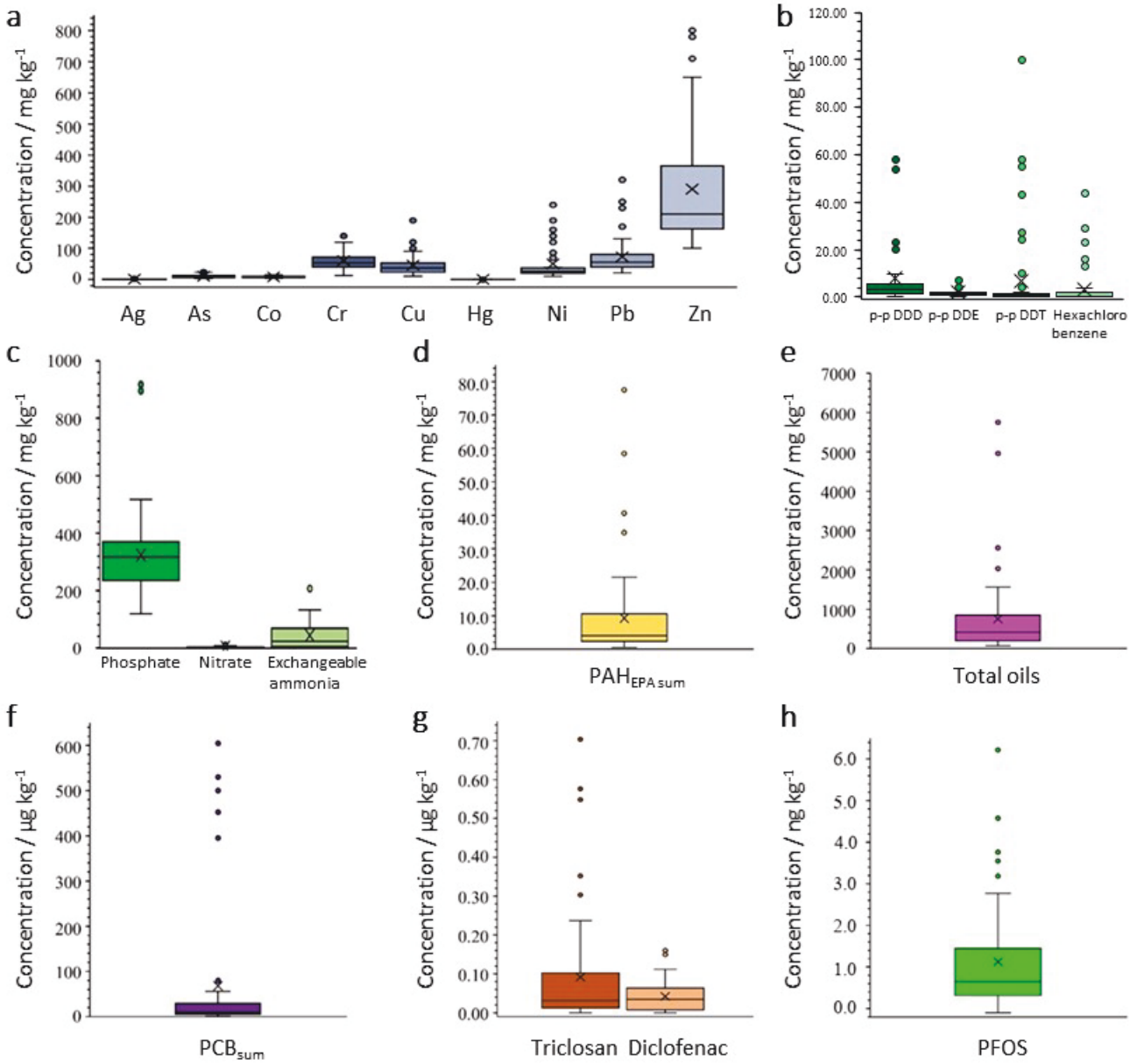


Fig. 2: Box plots for potential contaminants across all sites over the six sampling periods. Average, IQR range and outlier values for a) metals, mg kg^{-1}, b) pesticides, mg kg^{-1}, c) nutrients, mg kg^{-1}, d) total from 16 PAHs (PAH_{EPAsum}) mg kg^{-1}, e) total oils, mg kg^{-1}, f) total PCBs (PCB_{sum}) µg kg^{-1}, g) emerging contaminants, µg kg^{-1}, h) perfluorooctane sulfonic acid (PFOS) ng kg^{-1}, concentration in the sediment across each sampling site. In the boxplot, centre lines indicate the median and x shows the mean, n= 36 from nine sites, and 6 sampling campaigns.

3.2 Principal Component Analysis

PCA is a multivariate method that aids in interpreting complex data sets with regard to factors that govern variability among parameters and sites. It is applied here in order to identify the principal components (or factors) that account for the most variability within or among the sites.

A first PCA that was carried out across 78 variables, including geochemical and chemical parameters resulted in 14 principal components with an Eigenvalue above 1. The first 7 components accounted for a cumulated variability of the data of 76 % and showed high variable loadings for different sediment size fractions (data not shown) indicating that the different grain sizes contributed strongly to the overall variability. Chemical contaminants adsorb to sediment particles depending on the particles' surface area and surface charge, and are dominantly found in the <20 µm fraction (metals) and the <63µm fraction (organics). Consequently, concentrations were normalized to the respective dominant granulometric fraction for the next PCA, following Reid and Spencer, 2009.[22]

The PCA resulted in seven principal components with Eigenvalues above 1, whereby the first component explained more than 97% of the variability of all data (Table 2).

Table 2: Principal components with Eigenvalues >1, identified among 71 variables (metals and organic contaminants granulometrically normalized, standardized, log_{10} transformed).

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
Eigenvalues	2093.181	17.665	9.745	5.277	3.092	2.817	1.606
Percentage	97.468	0.823	0.454	0.246	0.144	0.131	0.075
Cum. Percentage (%)	97.468	98.291	98.744	98.99	99.134	99.265	99.34

On this component load the main variables identified were metals; Na, K, Al, Fe, Mg, Ca, but also total oils and available phosphate (Table S4.1). Thus, the sampling sites that were chosen differed a

lot with regard to their major elemental composition, which was originally intended when choosing the respective sites and regions.

Components 2 to 4 which allow differentiation between sites, figure 3 depicts the formation of clusters along the axes defined by PC 2 and PC3. The figure shows that the sites up and downstream of the WWTPs cluster together for each region (BE sites 1 and 2; UK sites 1 and 2; DE sites 2 and 3) while the sampling site at another water body (UK and BE sites 3) or, in case of the German site, in an upstream part of the river (DE site 1) differ from the other samples in terms of fine sediment (grain size fractions), the location in the estuary (Ca-signal), and nutrient supply (available phosphate) which all load onto PC2. More strongly are the differences along PC3, where at every region the sediments of one site differ from the two within the same catchment. With regard to Germany, the most upstream sampling site 1 differs from the two downstream sites. On PC2 load the variables phosphate (available), Ca, and fine grain sizes, all of which could reflect a gradient along a river with fine material transport.

Pesticides (HCH) and industrial compounds such as chlorobenzenes, furans, negatively load on PC3, and here, DE site 1 scores highly. Historically-produced industrial substances in the Elbe River derive mainly from upstream areas (Heise *et al.* 2008)[23], and result in highest concentrations at Site 1, while they become diluted with cleaner marine sediment further downstream at Sites 2 and 3. This contamination pattern is a little pronounced at Pocklington canal (BE site 3). This site seems to be little influenced by organic contaminants which caused the strong differences in the German samples. Zenne (BE site 3) cluster together and also negatively on PC3, indicating also here a stronger pollution compared to the sites 1 and 2, but different from the German site 1.

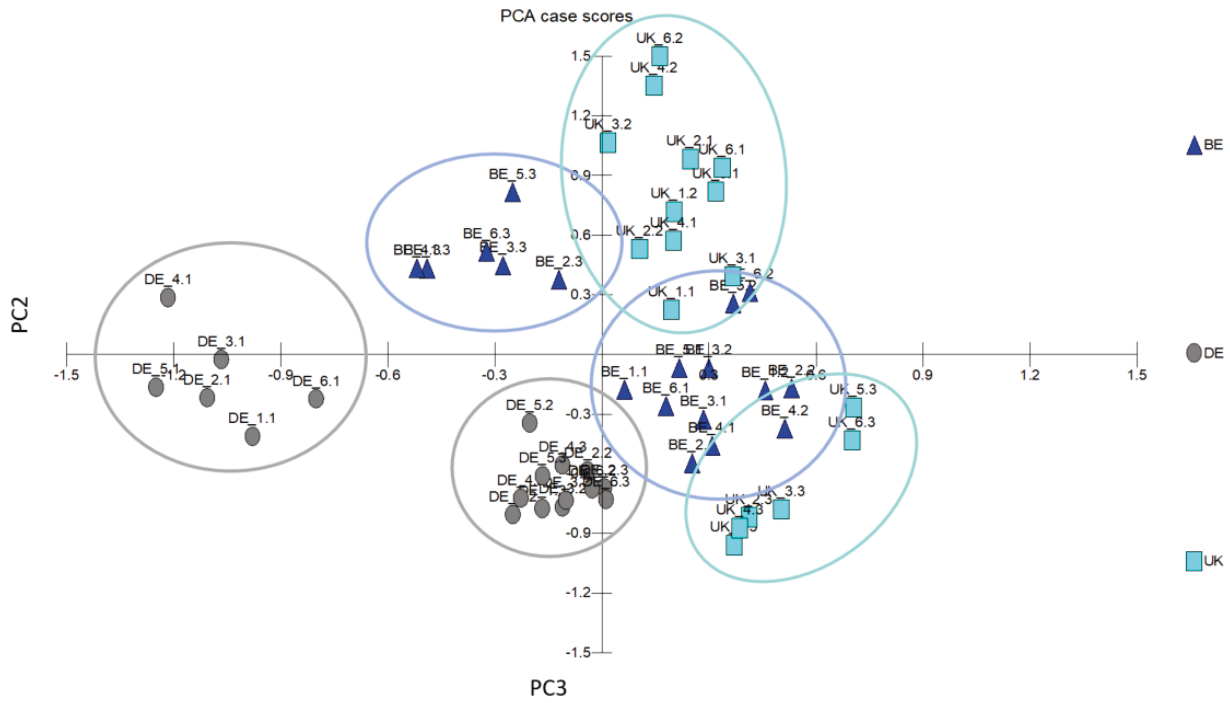


Fig 3: Case scores from PCA with 53 cases, 71 variables, organic contaminants and metals normalized for the respective granulometric fraction , PC2 versus PC3. The label of each sample identifies the region (DE – Germany, UK – United Kingdom, BE – Belgium), the sampling campaign (1 to 6) and, on the last position, the sampling site (1 to 3).

3.3 SQGQ calculations

Sediment quality guideline quotients were calculated using sediment quality guidelines determined by de Deckere *et al.*[21] to quantify the overall potential toxicity of each sediment based on 31 different components (Figure 4). Components studied included metals, PAHs, PCBs and pesticides. The concentration of each was compared to the guideline value, whereby a larger value suggests potential toxicity from that component. An overall value of 1 shows the potentially toxic nature of that sediment. This calculation showed that the Zenne had particularly high levels of contamination from many different components. The magnitude of toxicity varied across the sampling periods however, was consistently significantly higher than at any other site. All other sites, apart from site 2 and 3 (Köhlbrand and Wedel) on the Elbe, contained potentially toxic levels of contaminants during a number of the sampling campaigns.

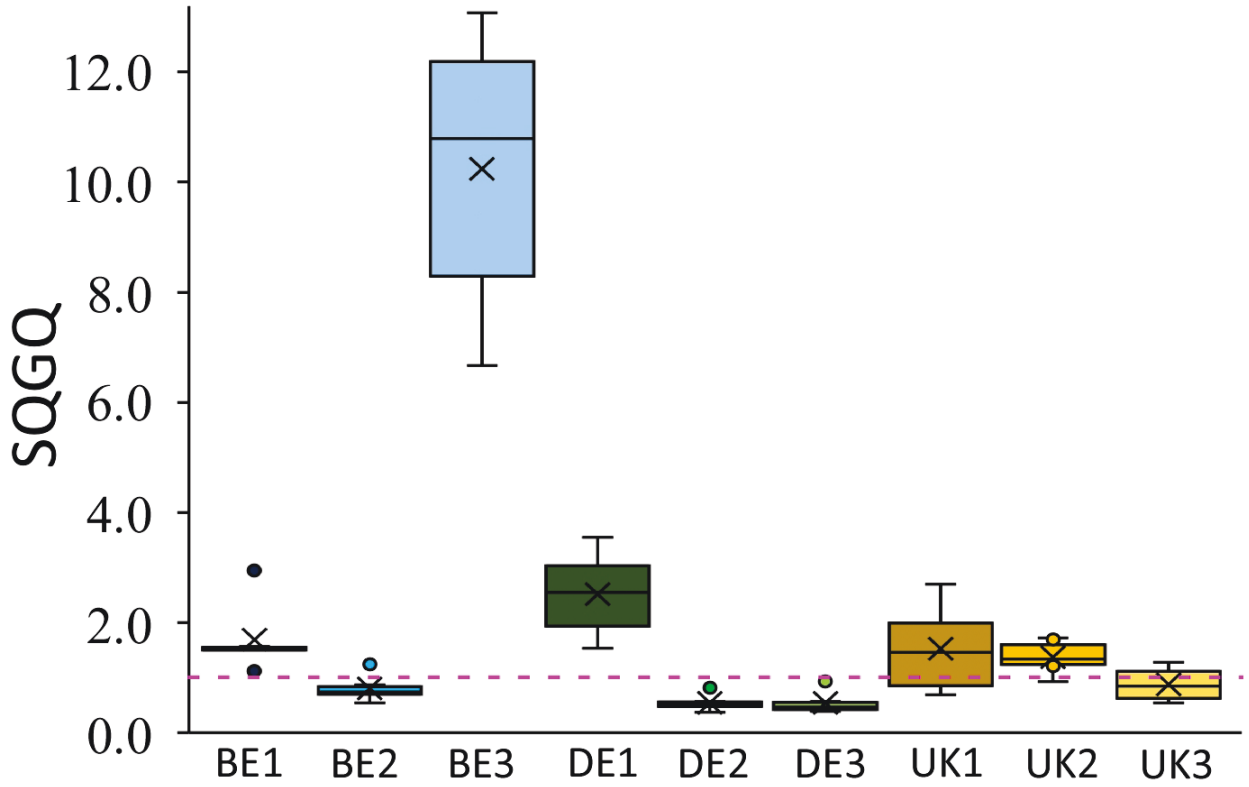


Fig 4: Sediment quality guideline quotient distribution for each site showing averages, range and outliers. In the boxplot, centre lines indicate the median and x shows the mean, n= 6. BE1 = Scheldt upstream BE2, = Scheldt downstream BE3 = Zenne, DE1 = Elbe, upstream, DE2 = Elbe WWTP, DE3 = Elbe downstream, UK1 = River Aire upstream, UK2 = River Aire downstream, UK3 = Pocklington Canal. The dashed line indicates a SQGQ value of 1, above this value would indicate potential toxicity of the sediment.

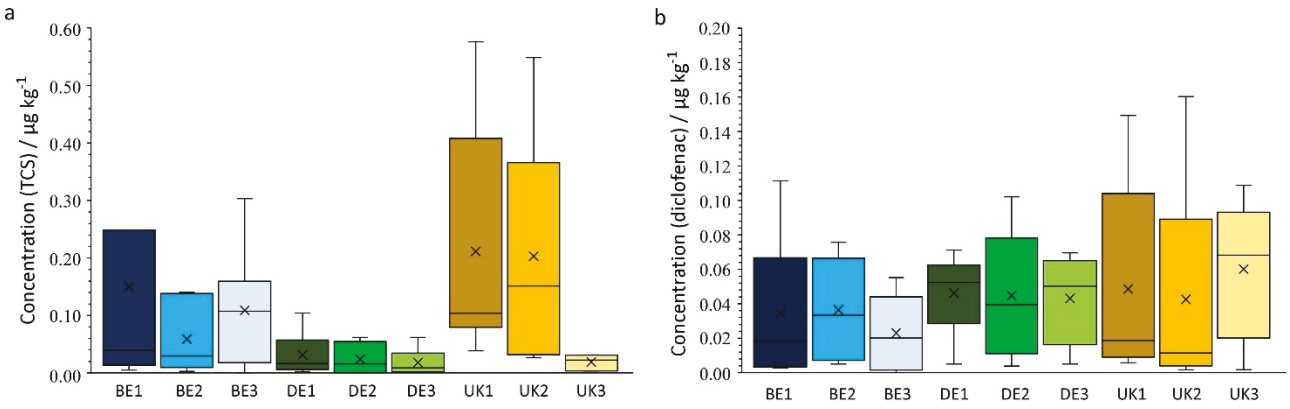
3.4 Emerging contaminants

Triclosan (TCS) and diclofenac (DIC) compounds were detected at all sites typically in the 0.01's to 0.1's of µg kg^{-1} range (Fig. 5). TCS sediment concentrations was found in most sites above 0.0019 µg kg^{-1} however showed large site to site variance (Fig. 5a), predominantly found at the two sites on the River Aire as well as the upstream site on the Scheldt. Average concentrations by site varied from 0.018 µg kg^{-1} (DE2 least contaminated site) to 0.21 µg kg^{-1} (UK1 most contaminated site). Of the two UK sites there was no statistical difference in concentrations found in the upstream or

downstream sediments (p=0.9453). DIC was also detected at all sites (above 0.002 µg kg^{-1}), with some variation was seen in the average concentrations found at each site between ranging from 0.028 µg kg^{-1} (BE3, least contaminated site) to 0.060 µg kg^{-1} (UK3 most contaminates site). Again the UK sites had the largest DIC load, with concentrations of up-to 0.16 µg kg^{-1} found in the River Aire. The concentrations of DIC in upstream and downstream sediments follow similar patterns to TCS and typically varied only slightly (UK2 and 3 site on the Aire, p 0.8685, BE1 and 2 sites on the Scheldt p = 0.927). These patterns are not reflected in other data sets for legacy pollution. Across most of the sample period, site BE3 is typically the most contaminated and UK3 one of the less contaminated sites, and downstream concentrations of contaminants are typically lower than upstream concentrations. This suggests that emerging contaminants may not follow patterns of legacy contamination.

Table 3: Average and range concentrations of the two emerging contaminates, TCS and DIC, recorded in all sediment samples with proposed regulatory values in sediment or freshwater for comparison.

Compound	**TCS**	**DIC**
Mean (µg kg^{-1}) dw	0.097	0.0429
Range (µg kg^{-1}) dw	0.0021 – 0.70	0.0021 – 0.160
Proposed EQS	Annual average environmental quality standards 24 µg kg^{-1} (Enviromental quailty standard). Sediment quailty criteria low 130 µg kg^{-1} and high; 3260 µg kg^{-1}. [24]	ESQ of 0.0054 or 0.23 µg L^{-1}[13] (sediment values not available)



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279 *Fig 4: WLCs a) TCS, b) DIC distribution for each site showing mean average, range and outliers. In the boxplot,*

280 *center lines indicate the median and x shows the mean, n= 6. BE1 = Scheldt upstream BE2, = Scheldt*

281 *downstream BE3 = Zenne, DE1 = Elbe, upstream, DE2 = Elbe WWTP, DE3 = Elbe downstream, UK1 = River Aire*

282 *upstream, UK2 = River Aire downstream, UK3 = Pocklington Canal.*

283 ## 4 Discussion

284 The analysis of such a wide range of containments in sediment has shown how different patterns

285 and pressures are present in different sediments. The sampling sites on the upper Scheldt were

286 situated in Oudenaarde. Site 1 (BE1) was located upstream and site 2 (BE2) 1.5 km downstream of

287 the WWPT Oudenaarde. Both sites plot close together on the PCA reflecting broader similarities in

288 physico-chemical characteristics (Figure 3), being predominantly fine-grained material, with relative

289 enrichment of Al, Fe, Ca and K indicative of clay-components of fine muds [24]. The site on the Zenne

290 (BE3) is located downstream of Brussels and characterised by enrichment in a range of potential

291 pollutants. The sites chosen along the Elbe Estuary in Germany were sampling site 1 (DE1) which

292 was located at Stover Strand, upstream of Hamburg at the most upstream area of the tidally

293 influenced estuary. Sediment mineralogy in these locations is known to represent a mixture of clay

294 minerals (e.g. smectite, illite, kaolinite) and carbonates (freshwater and marine) along a mixing

295 gradient in the lower estuary [25]. The site is influenced by polluted sediments coming from upstream

296 areas still bearing contaminant burdens from industrial and mining activities during the time of the

297 former German Democratic republic (GDR) and Czechoslovakia[25]. Sampling site 2 (DE2) was

located within the Hamburg Port area at the "Köhlbrand" immediately downstream of the discharge of the major Hamburg WWTP which serves a population of 2.3 million inhabitants from a catchment area of 300 km^2. Sampling site 3 (DE3) was located at Wedel, downstream of Hamburg. Both, DE2 and DE3, receive marine sediments that are transported upstream with the flood stream from the North Sea, as well as finer, potentially contaminated sediments from upstream, whereby due to the position of the sampling site, the percentage of marine sediment at DE3 is expected to be more pronounced due to its location further down the estuary. The River Aire and Calder is a heavily modified tributary of the Humber Estuary in the UK. It has a mixed land use with a high population density across the city of Leeds and surrounding towns. Historical mining (principally coal and lead) and a range of industrial activities (e.g. metal-works, hydrocarbon processing, textiles) have left a legacy of contamination of the river.[18, 26] Two sites on the River Aire, upstream (UK1) and downstream (UK2) of a major waste-water treatment plant (WWTP) serving ~1 million people, were selected to assess this range of historical and contemporary pressures. The sites are generally coarser in sediment size than other sample locations (given distance ~30km upstream of the tidal limit) with mineralogy known to be dominated by clays and carbonates (reflecting glaciated terrain and underlying Carboniferous strata in headwaters) with enrichment of a range of anthropogenic minerals (e.g. barytes, fluorite and high temperature minerals such as slags: [27]). The other UK site is the Pocklington Canal (UK3), a typical, heavily-modified lowland rural site with known nutrient enrichment and high organic matter content. issues.

Across these three catchments and nine sites studied there was a wide variation in the types and nature of contaminants present, as expected when choosing sites with varying geographic pressures and historical contamination (Fig. 1). This site-to-site variation in geochemistry was found to largely explain the differences in pollution pressures seen (PCA analysis, SI section 3.2; SI 4) and clustering by site reflects the limited effect of seasonality on contamination pressures. The sites chosen on

322 the upper Scheldt (Belgium) have been historically contaminated with a mix of contaminants
323 including potentially toxic metals, PCBs and pesticides. The Zenne represents a water body with
324 known contamination of a wide range of Priority List substances from a range of industrial sources
325 and pathways, including contaminated groundwater discharge to the river [28].

326 The majority of sediments contained some elements or compounds at concentrations that could be
327 potentially hazardous; typically, site BE3 (Zenne) had high concentrations from all analyte groups.
328 Other sites on the Scheldt where particularly high for metals and PCBs, in contrast sites on the Elbe
329 typically contained higher concentration of metals and pesticides, with only site DE1 showing high
330 levels of PCBs. UK sites along the river Aire also had metals present above exceedance levels but
331 also PAHs which were found in other sites in such high concentrations. Despite this prevalence of
332 contamination at each site, very few samples contained contaminants from every group at higher
333 levels. This shows the importance of understanding the varied chemistry that may be present to
334 fully characterise the contamination characteristics that could be considered potentially toxic. The
335 PCA analysis (section 3.2) demonstrated the relationship between fine sediment material and a wide
336 range of potential pollutants. There was a wide range of indicators identified by PCA analysis, fine
337 material (<63 µm), pesticides, PCBs, butyltin-compounds (except dibutyltin), PFOS, Furans,
338 industrial metal(loid)s (As, Cd, Hg, Co, Zn) accounted for 32 % of variation from the dataset. The
339 ubiquity of per- and polyfluoroalkyl substances in samples across the sites, irrespective of land use
340 variation reinforces a pattern that is becoming increasingly apparent in many recent studies [29]. This
341 further supports the need for a broad analytical investigation of sediment quality, rather than focus
342 on a few key groups.

343 To characterise the overall toxicity of each site sediment quality guideline quotients were produced
344 using 31 contaminants, with existing PEL values (Fig. 4). Whilst this was not an exhaustive
345 assessment of the full data set, it did represent a range of contaminants: metals, PAHs, PCB and

pesticides. These compounds are known to affect some of the study sites historically. The site on the Zenne was shown to be particularly toxic, with concentrations widely exceeding the PEL values on multiple occasions, this was not a surprising result as it is well documented that the Zenne has significant pollutant pressures, even with recent improvements made to WWTPs in the area.[30] ~~[2]~~ [31] The upstream site on the Scheldt and the Elbe also had high levels of contaminants (eg. PCBs) that would indicate these sediments were potentially toxic to sediment dwelling organisms during the study period. All other sites showed some indication of toxicity at least once of the sampling periods. The range shown in these SQGQ calculations does suggest some variation in contaminant concentrations across the sampling period (SI section 5, figures SDI 5.1 – 5.6) suggesting the sediment is a dynamic environment with the potential to release these contaminants into the water stream should sufficient agitation of the sediment occur.

The sediment quality guideline quotients give an indication of a sediment's potential hazard and can help to explain measured toxicities at a site. But they have a number of limitations: 1) there is a lack of widely adopted regulatory values for many compounds in freshwater sediments. 2) The PEL that were derived by de Deckere *et al*.[21] are based on a large data set of ecotoxicological data. Nevertheless, they cannot predict how available contaminants are at a specific site, as this depends on e.g. the age and history of pollution. 3) They cannot take mixture toxicities into account. 4) They can only be calculated if chemical components were analysed. Thus, they fail to identify if there are key components that are adding toxicity. If an overall assessment is based on the summation of sediment quality guideline quotients, a large excess of one contaminant or a small excess of many contaminants could appear to give the same overall toxicity of a sediment. However, dealing with one set of contaminants in a sediment is very different to managing a complex mixture of sediment-bound pollutants. To understand this, individual components were compared to their respective

regulatory values, particularly for PCBs and PAHs, which represented the two chemical groups which are often measured as total concentrations.

Whether considering total PCB's or individual PCBs (shown in SI section 5, fig. 5.3 and 5.4) the patterns are the same, concentrations are high in the Zenne, where all concentrations exceed both PEL and TEL (Threshold Effect Levels) regulatory values. Higher concentrations of total PCBs, exceeding TEL values, were also measured in most sites, excluding the Pocklington Canal, for at least one of the sampling campaigns. However, if each PCB is compared separately the pattern can be quite different. For example, for PCB28, most sites exceeded both PEL and TEL guidelines across the whole sampling period (Appendix, Supplemental Information Figure S5). Despite this being the PCB that was detected at the lowest concentrations (< 10 $\mu g\ kg^{-1}$), it could be considered the one posing most toxicity due to the consistent breach of the TEL and PEL limits. This information is not readily gained from the PCB totals and therefore may suggest measuring and reporting individual contaminants has value in understanding sediment toxicity.

Individual PAHs were also compared to their respective TEL and PEL limits, as shown in the Supplemental Information Fig SI5 and 6. PAHs were detected in all sampling locations at varying levels which would not be considered unusual; PAHs are still seen as one of the most widespread [34] and persistent [35] environmental pollutants All PAHs were recorded in the Zenne at levels always above the TEL values and often exceeding PEL values too. The UK sites also had higher levels of some PAHs, both sites on the River Aire, and less frequently, the Pocklington Canal had concentrations exceeding those advisory values. The River Aire has known legacy contamination of PAHs, such as benzo-a-pyrene from a range of legacy sources associated with coal mining, power generation and gasworks, therefore it is unsurprising to find the existence of elevated levels of other PAHs.[36] However, it is less well documented that such contaminants exist in the Pocklington Canal, a water body that is generally viewed as clean with most major issues linked to historical nutrient

enrichment. This study indicated the presence of many PAHs in the Pocklington Canal sediment at concerning concentrations, typically above the TEL levels, even exceeding PEL levels on several occasions.

Contamination from metals (Fig. SI 5.2) has previously been identified at most sites, a legacy from industrial periods, urbanisation and mining.[18, 37, 38] Unlike other chemical groups the distribution of metals varied between the countries and sites. Chromium was found in high concentrations in Site BE1, whereas mercury was present in high concentrations in the Zenne and Elbe catchment (site DE1), lead was also found at high concentrations in the Zenne. In contrast, the Aire showed comparatively lower concentrations in that the upstream site contained all three metals of interest, typically above TEL and occasionally exceeding PEL limits, whereas the downstream site had lower concentrations typically between PEL and TEL values, which may reflect upstream geogenic and lead mining sources in headwater areas.[26]

Previously considered contaminants are typically well defined and included in Priority Lists due to their ubiquity in urban and post-industrial catchments alongside their potential toxicity. This study also examined the presence of emerging contaminants in the sediment, specifically triclosan (TCS), diclofenac (DIC) and oestradiol (E2). It was found that E2 was not present in most samples with the exception of one site in the Humber catchment. TCS and DIC were found in most sediment samples in the 10's ng kg^{-1} range. TCS concentrations varied between the sites, with highest concentrations typically found in UK sites, on the River Aire and in the Belgium sites (Figure 4a). Interestingly, there was not so much variance in concentrations between sites upstream and downstream of WWTP. This may reflect other upstream sources for TCS which could include other WWTPs and suggests a broad distribution across the catchments studied. DIC concentrations were largely consistent at all sites, although concentration varied with sampling considerably (Figure 4b). The concentrations found in the sediment can be compared to those reported by Kay *et al.,* 2016[11] who reported DIC

levels at 100's ng L^{-1} in the River Aire.[11] Although synchronous monitoring of water column and sediment concentrations are a clear research requirement, the difference in order of magnitude presented herein suggests there is minimal partitioning of DIC to near-field sediments around known WWTP inputs. As such there are very limited regulation of guidelines for these compounds, however they were all detected at very low levels, and relevantly, for TCS, Amorim *et al.,* in 2010, proposed limit of 0.8-4 μg kg^{-1} [394] which is far higher than any of the concentrations detected at any site in this study.

5. Conclusions

The three catchment areas and nine sampling study sites reflect a high variation including those with large urban population and influence of effluent of waste-water treatment plants coupled with historic industrial processes and urbanisation pressures, contrasted with rural sites with typically low historical contamination. This study highlights the relationship of fine sediment material with large and varied pollutant enrichment from contaminants, butyltin compounds, metal(iod)s, PCBs, pesticides and several other organic compounds (including PFOS). The key indicator compounds described reflect the historic industrial pressures that continue to affect several waterways where ongoing dredging operations are impacted by the potential presence of pollutants. This is especially seen in the Zenne, where potential toxicity of the sediment was determined using sediment guideline quotients. These were frequently above 1 for a wide range of compounds within the sediment. Most other sites also showed indicated some hazard, exceeding guideline values on more than one occasion, typically for a wide range of analytes including metals, pesticides, PCBs and PAHs. Whilst the extent of potential toxicity was most extreme for the Zenne, the data reflects the

historical industrial pollution that affects most of the waterways, likely the legacy of stored contaminants within the sediment. The presence of multiple contaminants demonstrates the importance of analysing for a broad selection of potential contaminants to truly characterise the chemical mixtures present in sediments and therefore appropriately manage it. This study also explored the presence of emerging contaminants, triclosan and diclofenac demonstrating their presence in the sediments and their accumulation before and after WWTP's, a pattern not typically observed with legacy contaminants.

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