Current Trends in Analytical and Bioanlaytical Chemistry

Review Article   **Open Access**

Organic Pollution in Surface and Core Sediments from the Yangtze River Estuarine Region - Historic Research Study and A Review of Recent Investigations

Peter J Baugh[1,2]*, Simon M Hutchinson[3], Liu Min[4], Lizhong Lu[4], Weigou Zhang[4], Su Xu[4], Claire McGill[5], Helen Ball[5], Brian Ward[5], Daniel Marshall[5] and Radja Bougherira[5]

[1]Environmental and Food Analysis Special Interest Group, The British Mass Spectrometry Society, UK

[2]University of Chester, UK

[3]School of Environment & Life Sciences, University of Salford, UK

[4]Key State Laboratory for Estuarine and Coastal Research, East China Normal University, Shanghai, China

[5]Department of Chemistry, University of Salford, Salford, UK

Abstract

The surface and core sediments obtained from the Yangtze River-south coast estuarine region, and analysed by GC/MS after sample preparation, exhibit a range of organic pollutants over depths from the surface to 0.5 m. The target organic compounds identified are in following categories, homologous series of hydrocarbons, polyaromatic hydrocarbons (PAHs) and linear alkylbenzenes (LABs), Individual compounds -N, N-diethylamide-3-methyl benzamide, phenyl-β-naphthyl-amine, chlorinated benzenes, 2,6-diisopropyl naphthalene (2,6-DIPN) and compound classes deriving from human waste - sterenes, indicative of sterols.

The PAH concentrations range from 12 μgkg^{-1} to *ca* 1.87 mgkg^{-1}, of the order expected. Furthermore, in addition to core sediment, surface sediment (and vegetation) show a surfeit of LABs originating from detergent waste - both domestic and commercial, varying in concentration from 0.2 to 26 mgkg^{-1}. The concentrations of selected individual pollutants determined range from sub gkg^{-1} to *ca* 100 mgkg^{-1} (phenyl-β-naphthylamine).

There is the possibility of hormone mimicking behaviour (endocrinal activity) for compounds originating from human waste at the concentrations observed in intertidal surface sediments ranging from 0.1 to 73 mgkg^{-1}.

The integrity of the sediment in terms of the extent of pollution is considered by comparison with estuarine regions, worldwide.

The analytical methodology for the preparation of sample extracts suitable for analysis by GC/MS is described. The use of the data system for identification via a mass spectral database (NIST) and quantitation via selected analysis of selected single mass ions are outlined. The validity of the data obtained is discussed.

A review of more recent and current investigations is included to complement this historic investigation.

Keywords

Yangtze river, Organic pollution, Intertidal surface, Water, Sediment, Characterisation and Quantitation, GC/MS analysis

Introduction

Estuarine and coastal regions world-wide are subject to pollution by inorganic and organic substances to varying degrees depending on the extent and type of anthropogenic activity in the immediate environment and the catchment of the estuary. Specifically, the organic pollutants stem from industrial, rural and marine sources and/or domestic sources; human and household waste products. The contamination of sediments in estuarine and coastal regions by PAHs, in particular, has received wide attention [1-6], and studies have involved determination of the distribution in core and surface sediments, deposition rates and depth profiling [7].

Obtaining a fully authenticated profile of the nature

Figure 1: Sampling sites for sediment and vegetation taken from the Yangtse River -South Coast Estuarine Region. **Mainland**: **(A)** Fu Qiao; **(B)** Bao Shan; **(C)** Wu Song Kou; **(D)** Bai Long Gang; **(E)** Dong Hai Nong Chang and Suzhou Creek in the vicinity of Shanghai. **Island**: Chongming. **Lines**: blue -rivers/lakes; Black -roads between towns.

of organic substances and the levels of targeted pollutants in sediments sampled within the estuarine region can often present an almost overwhelming and impossible task for the analyst for a variety of reasons.

Thus, any study that attempts to progress beyond the characterisation/identification stage to a full quantification profile of organic targets can founder because of an inability to sample effectively and rapidly analyse the sample extract. Furthermore, although depth profile data can be obtained within core sediment samples, attempts to probe associated stratification distribution may be hampered by the lack of adjacent core sampling. Re-investigation of hot-spot areas is restricted by logistics and shifting sediment, particularly in dynamic environments. The focus here is on the significant features with an indication of how widespread the pollution, general pollution where significant, unique targets - environmentally, toxicologically and biologically hazardous substances and human waste substances of hormonal active type of significance to aquatic life, including fish.

The Yangtze River (Changjiang) delta region has a population of over 100 million. The high population density, centred on Shanghai, the concentration of industry

and infrastructural improvements, which have routed effluent discharge directly to the coastline [8], render a potentially high environmental impact of pollution upon the Yangtze Estuary. There had been relatively little information available concerning coastline contamination in this region up to the date of this study [9,10]. A surfeit of more recent studies provides an insight into the coverage of sediment pollution in this region (see review, page 8)[a].

---

[a]A useful general reference on the determination of organic compounds in soils, sediments and sludge has been published, see Crompton [11].

*Corresponding author: Peter J Baugh, FRSC, Leader, Environmental and Food Analysis Special Interest Group, The British Mass Spectrometry Society, UK; Visiting Professor, University of Chester, UK, E-mail: peterbaugh682@hotmail.com

Study Area

The tidal flats on the southern bank of the Yangtze Estuary have developed under the interaction of river flow and tidal waves with the latter dominating seaward. There is generally no super tidal zone due to extensive land claim. The vegetation has low floral diversity, with reeds dominating in the upper part and *spartina* grasses in the upper to middle parts of the tidal flats.

A prime aim of this study was to characterise, in general, the organic pollutants over a range of core and surface sediments taken from selected sites along the South Coast of Yangtze River Estuarine Region that are representative of the several environments, as described in the experimental section, under sediment.

Experimental

Sediment

The sediment samples were obtained by surface scraping and core extraction using a Livingston stainless steel piston corer from five sites located along the South Coast Estuarine Region of the Yangtze River (Figure 1). The sites sampled are summarised as follows:

1. Fu Qiao, site A, a rural region to the north, largely uncontaminated.

2. Bao Shan, site B, a region with steel works and sewage outlet.

3. Wu Song Kou, site C, at the head of the Huangpu River.

4. Bai Long Gang, site D, a region with sewage outfall.

5. Dong Hai Nong Chang, site E, a rural region, slightly contaminated.

All sites were sampled in 1995 and 1996 except for site A that was included in 1995 only. Several other sites have also been monitored, notably Suzhou Creek, 1996 and 1997 and islands, namely, Chongming Island, and Jiu Duansha, that was established and newly formed in the estuarine region.

Standards, solvent and reagents

The internal and volumetric standards were obtained as follows: mirex and decachlorobiphenyl from British Greyhound; deuterated naphthalene, biphenyl, phenanthrene and anthracene from Aldrich Chemical Co. Solvents - hexane and dichloromethane for extraction, anhydrous sodium sulphate reagent for drying of extracts and analytical grade reagents were all obtained from Fisons Chemicals Ltd. Authentic reference compounds for some target analytes were obtained from Aldrich Chemical Co, namely, phenyl-β-naphthylamine, N, N-diethylamide-3-methyl benzamide, hexachlorobenzene and selected PAHs.

Preparation of extracts from Sediment samples

The intact core samples were dissected into 1 cm sections and air dried at 50 °C in a thermostated oven. The surface sediment samples were not dissected but air-dried as above. Sieving of the sediment was deemed unnecessary in view the fineness of sediment grain.

For quality control purposes all samples of sediment were spiked with 1 cm³ volumes of internal standards at a concentration of 1-2 mgL⁻¹ equivalent to 0.2-0.4 µgg⁻¹ spiked sediment. The internal standards employed were mirex as a general purpose internal standard, but particularly for organochlorine compounds (pesticides) and in selected instances deuterated analogues of PAH, d_8 naphthalene and d_{10} phenanthrene. Volumetric standards, decachlorobiphenyl (1 cm³; 1 µgcm⁻³ in the final extract volume), d_{10} biphenyl, d_{10} anthracene (1 cm³; 2 µgcm⁻³) in hexane were added at the final extract stage to provide an accurate final volume of 1 cm³ after resuspension.

Pre-extracted sediments were used as controls for the recoveries of the internal standard and a selected range of priority pollutant standards in order to validate the extraction and analytical methods.

Extraction was effected by placing the sediment samples (5 g) spiked with the internal standards (concentrations as specified above) in small round-bottomed flasks (250 mL) located in an ultrasonic bath, adding 3 successive volumes of hexane: dichloromethane (20 cm³: 50: 50) solvent mixture and sonicating for 30 min. The extracting solvent at each stage was passed through a porosity No. 4 glass sinter charged with sodium sulphate. The combined extracts (60 cm³) were rotary evaporated to a small volume (< 10 cm³) and then to dryness in a small tube using dry N_2 cylinder gas. 1 cm³ of a selected volumetric standard (1 µgcm⁻³ of decachlorobiphenyl (DCBP), 2 µgcm⁻³ of d_{10} biphenyl and d_{10} anthracene) was added to ensure accurate determination of the analytes of interest and the recoveries of internal standards added for quality control purposes[b].

Vegetation (1 g), previously air-dried and ground to a powder was treated according to the procedure above and spiked with internal standards at a concentration of 1 µgg⁻¹ of vegetation. The data obtained is stated in the results and discussion but not included here.

Known concentrations of reference compounds were used for the determination of the levels of PAH pollutants; d_8-naphthalene and d_{10}-phenanthrene were employed as

---

[b]It should be noted that the methodology employed for sediment using solvent extraction and GC/MS for analysis provides an alternative to that described in EPA Method 8275A [12], which was designed for semi-volatile organic compounds, in particular, PAHs and PCBs, in soil/sludge and solid wastes, and, which employs thermal extraction GC/MS.

Table 1: % Recoveries of the internal standard- mirex, added to core sediment sections from Bao Shan (Site B), Bai Long Gang (site C), and a selected range of priority pollutants added to core sediment originating from Dong Hai Nong Chang (site E).

Core sediment Sample, Depth, Cm	% Recovery of mirex	Priority pollutant recovered	% Recovery[a]
Site B		**Site E**	
35	105.6	Acenaphthalene	90
35	107.6	Anthracene	68
35	85.3	1,3-Dichlorobenzene	125
Site C		1,2-Dichlorobenzene	150
1	84[a]	Diethyl phthalate	116
3	84	Hexachlorobenzene	82
5	134	Pyrene	132
7	111		
9	100		
13	146		
17	68		
25	38		
53	103		

[a]single point determination.

internal standards and d_{10}-biphenyl and d_{10}-anthracene as volumetric standards. First, calibration curves were obtained from plots of relative response factor (RRF) (reference compound area/volumetric peak area against reference concentration) and then the concentrations of analyte compounds were determined using the calculated RRF. The plots approached linearity with correlation coefficients in the range, 0.98-0.99. The limit of detection for individual analytes was estimated to be 0.01 mgkg^{-1}.

Analytical quality control (AQC)

To determine the recoveries of the organic compounds identified, the internal standard - mirex at a known concentration (1 cm^3; 1 μgcm^{-3}) was added to the sediment samples prior to extraction. The determination of the concentration of the internal standard in the final extract and comparison with the concentration added initially allows determination of % recovery of the internal standard. Table 1 summarises the quality of the recovery of the internal standard over a range of core sediment section extracts analysed and originating from sites B and C. Furthermore, analysis to validate the quality of the extraction and recovery was carried out. The procedure involved spiking pre-Soxhlet extracted sediments from a clean site E with a selected range of EPA priority pollutants (1 cm^3; 5 μgcm^{-3}) that are representative of organic pollutants identified. Table 1 also summarises the % recoveries of these priority pollutants that in the main fall within the range of ca. 70-120% in agreement with the recovery window specified by US-EPA in quality control protocols. The target compounds have not been spiked into sediments to directly obtain % recoveries but are reasonably assured by reference to those of the priority pollutant standards (Table 1), for example, for PAHs detected, the EPA standards are acenaphthalene, anthracene and pyrene, and for the chlorobenzenes detected, the standards are 1,2-, 1,3- and hexa-chlorobenzenes[c].

Table 2: Gas chromatography and mass spectrometry operating conditions for analysis of sediment sample extracts.

1. Gas chromatography	Hewlett packard 5890
Carrier gas	Helium. Ultra-high purity, 99.9995%; 5 psi
Initial temperature; Time	55 °C; 2 min
Ramp rate	15 or 20 °C min^{-1}
Final temperature; Time	300 °C; 2 min
Injection volume	1 μl
Injection mode	Splitless, hp autosampler model 7673A
Injector temperature	270 °C
Capillary column	J & W DB5-MS 30 × 0.32 mm; Df = 0.25 μm
GC/MS interface temperature	270 °C
2. Mass spectrometry	**Fisons instruments trio 1000**
Source temperature	250 °C
Ionisation mode	Electron impact
Electron energy	70 ev
Emission current	150-200 μA
Mass scan range	4-550 u
Scan time	0.9 sec
Resolution	Unit mass accuracy

Analysis by GC/MS

Gas chromatography-mass spectrometry in electron impact mode was used to characterise, identify and quantify the organic pollutants. The features of the GC/MS facility and conditions employed are provided in Table 2.

Mass spectral methods for the identification of organic pollutants

Table 3 summarises the features of the organic pollution of the sites monitored, 1995-1998. As a first step

[c]AQC, in general, is well-documented in the EPA handbook for water and waste water laboratories, 1979 (EPA-600/4-79-019) [13].

Baugh et al. Current Trends Anal Bioanal Chem 2018, 2(1):64-73

ISSN: 2642-4266 | • Page 67 •

Table 3: Features of the organic pollution of the sites monitored, 1995-1998.

Type of organic pollutant	Site	Year	Type of sample
A. Homologous series			
Polynuclear aromatic	Bao shan, Site B	1995/96	Core sediment
Hydrocarbons	Suzhou creek	1997	Core sediment
	Wu song kou, Site C	1995/1996	Core sediment
Linear alkyl benzenes	Bao shan, Site B	1995/1996	Core sediment, Surface sediment Vegetation
	Dong hai nong Chang, Site E	1995	Surface sediment
B. Unique organic compounds			
Hexachlorobenzene	Bao shan, Site B	1995	Core sediment, 17-43 cm depth
Phenyl-β-naphthylamine	Wu song kou, Site C	1995	Core sediment, Localised at 57 cm
	Jiu duansha island	1998	Core sediment
N, N-diethylamide-3-methyl benzamide	Wu song kou, Site C	1996	Core sediment, 1-13 cm depth
Dichlorobenzene	Suzhou creek	1996	Core sediment, Depth 15-30 cm
2,6-diisopropyl naphthalene	Bao shan, Site B	1995/96	Surface sediment
C. Human waste/Hormone related			
Sterols indicated by sterenes	Site C	1996	Core sediment
	Suzhou creek	1998	Various depths
	Sites B, C, and D	1995	Surface sediment

to the identification of compounds present mass chromatogram data processing was conducted to determine if particular compounds or compound classes are present. This technique requires a prior knowledge of the fragment ions of selected mass (m/z) that are characteristic of types of known compound that are candidates for the pollution. A list of fragment ions selected with the compound and compound classes they represent is summarised in Table 4. The organic compounds represented feature in sediment and vegetation extracts originating from samples taken predominantly from the contaminated sites.

The unique compounds found in selected core sediments were not identified by this method (see also Table 3). The presence of these organics (and other compounds not targetable by mass chromatogram analysis) was obtained by routine data processing of each chromatographic peak in order to match the mass spectrum observed to the mass spectral data base and in specific instances the use of authentic reference compounds. The fit match factor in each instance was sufficient to provide reasonable confidence in the identification of these organic compounds.

Retention index analysis and matching

Mass spectral matching can be ambiguous particularly when applied to structural isomers which have virtually identical mass spectra, such as PAHs or a homologous series for which the mass spectra are extremely similar in spite of differences in RMM, for example LABs. In these instances, linear retention index matching is required to reference the particular isomer or homologue. Here, a range of n-alkanes, C_{15} to C_{20} with linear RI, 1500 to 2000 and selected PAHs were employed to compute the linear

Table 4: Selection of characteristic fragment ions (m/z) for mass chromatogram analysis to target organic compounds in the GC/MS total ion chromatogram (TIC).

Fragment ion mass selected, m/z	Compound or Class represented	Compound group in sediment extracts
91, 105, 119	Alkyl benzenes	LAB
		LAB
128, 142	Alkyl naphthalenes	PAH
149	Phthalic acid alkyl esters	Plasticisers
164	Azulene	Aromatic
168	Benzofuran	Aromatic compound
170	Trimethyl naphthalene	Alkyl Pah
178	Anthracene phenanthrene	PAH
192	Methyl anthracene	Alkyl PAH
202	Pyrene/Fluoranthene	PAH
228	Chrysene benzanthracene	PAH
252	Perylene	PAH
191	N,N-Diethylamide-3-methyl benzamide	Insecticide
219	Phenyl-β-naphthylamine	Corrosion inhibitor
205, 220	Bis-phenol A and related compounds	Antioxidant
188	Benzophenone	Additive
210	Hexachlorobenzene	Pesticide

RI for LABs [14-16]. Table 5 summarises the linear RI data for LABs.

Characterisation of the LABs indicates a range of homologues in the C_{18} to C_{20} carbon number bracket matched through RI data (n-alkane based) which are in agreement with the literature for LABs detected in es-

Baugh et al. Current Trends Anal Bioanal Chem 2018, 2(1):64-73

ISSN: 2642-4266 | • Page 68 •

Table 5: Linear retention index matching for LABs in selected core sediment sections (elected site - Bao Shan, core B2).

LAB	Ions, m/z	I_{obs}^{a}	I_{Lee}^{b}	I_{Lee}^{c}
1,3,5-trimethyl	91, **105**, 120	735	n/a	n/a
1-butyl heptyl	**91**, 147, 175, 232	1627	281	278.6
1-pentyl heptyl	**91**, 105, 246	1719	295	293
1-butyl octyl	**91**, 105, 246	1724	296	293
1-ethyl decyl	**91**, 105, 246	1758	300	298.6
Aromatic	91, **179**, 246	1761	301	n/a
1-methyl undecyl	**105**, 246	1798	307	304.5
1-hexyl heptyl	**91**, 260	1820	310	308.3
1-pentyl octyl	**91**, 260	1822	310	308.5
1-butyl nonyl	**91**, 147, 260	1826	312	309.5
di-isopropyl phenyl (isomer)	**223**, 238	1890	321	321.2
di-isopropyl phenyl (isomer)	**223**, 238	1920	326	326.7
4-phenyl bicyclo hexyl	91, **117**, 159, 173, 242	1965	333	n/a

[a]n-alkane RI; [b]Lee calculated in this work; [c]Lee literature values, reference [14].

tuarine sites elsewhere [15] and in particular Fox River, Wisconsin. Interestingly, although ambiguity in mass spectral matching might be expected because of the similarities in fragmentation pattern there is a direct correlation between RI and mass spectral match via the NIST data base for the LAB homologous series over this limited carbon number range.

Results and Discussion

General features of organic pollution of sediment sample extracts

The chromatographic profiles of extracts from sediment samples originating from the different sites vary in degree and complexity of pollution. The sites exhibiting the highest level of pollution as expected are Sites B, C and D that are adjacent to domestic and/or industrial-commercial sources. Sites A and E are largely free from the major pollutants observed at Sites B, C and D and can be used as controls. The Suzhou Creek site (1997) and estuary island sites (early stage of analysis, 1998) show some features in common with the contaminated sites. Table 3 summarises the class of compound, the uniqueness of the compound found, the location, date and type of sample, e.g., core or surface sediment or vegetation with general details of depth of detection. It can be seen that the organic pollutants can be split into three main groups. Although homologous series of hydrocarbons are also detected widely in the sediment samples analysis of these groups has not been targeted here.

Determination of the level of pollution by organic compounds

Homologous and related series: The approximate concentrations of the organic compounds identified can be determined by comparing the response relative to that of a known concentration of a volumetric standard to the response of a known concentration of the internal standard which is selected to be representative of the target compound (or compounds) relative to that of the same volumetric standard. The mass spectrometric responses of the target compounds depend on the % abundance of the base ion (100% RA) used in quantitation (related to the % ion current carried). The response can vary by a significant factor, particularly when compared to that of a single internal standard. Mirex (base ion peak quantified, m/z, 272) was employed as a general purpose internal standard and calibrated against the volumetric standard, DCBP (base ion peak m/z, 498). LSQ equations obtained were typically, y = $0.88 \times +0.312$, $0.259 \times +0.56$, $1.088 \times +0.153$ with $r^2 = 0.984$-0.995 (S.D. = 5.85×10^{-5}, RSD = 0.59%).

Depth profiles were obtained for selected PAHs that highlight the sections within core samples over which the pollution extends. Generally, the pollution decreases with core depth consistent with expectation on the basis of rates of sediment deposition (according to a recent survey the rate varies from 2-3 cm to 15 cm per year in this region and is dependent on the environment of the site monitored [17]). Absolute values can only be estimated if the rates of accumulation (adsorption and biological) and biodegradation are known either of which may be favoured depending on the half-lives of the pollutants. The results reflect the increase in anthropogenic activity in recent years. In a comprehensive study by members of the group, Min, et al. [7] have reported a detailed analysis of the depth profiles for PAHs in core sediment samples taken during this period. The range of concentrations of selected organic pollutants, 12 μgkg⁻¹ (trimethyl naphthalene) to 1.87 mgkg⁻¹ (anthracene) representative of that obtained for the polluted site B, Bao Shan, is summarised in Table 6 and Figure 2 illustrates the composition of PAHs at a depth of 11 cm. A typical total PAH profile (summed concentrations) for core sediment sections examined over depths of 1 to 47 cm is illustrated in Figure 3; note that at a depth of 11 cm the total PAH concentration is almost maximal (only greater at 19 cm).

Baugh et al. Current Trends Anal Bioanal Chem 2018, 2(1):64-73

ISSN: 2642-4266 | • Page 69 •

Several selected references are also of relevance here with regard to more recent work on the analysis of PAHs in sediments and other matrices, in other locations and

are exemplified by Barcelo, et al. [18] and Cheng, et al. [19], in relation to the validation of the results obtained.

LABs are prevalent also in core sediments from the more polluted sites, and of seven identified only two were identified near to the surface while the other five were found at increasing depths. Four of the more deeply distributed LABs were found also in surface sediment and have been reported as being present in sediment samples taken from the Fox River system [16]. The LABs appear to be concentrated at a depth of about 9 cm. The variation in concentration with core depth suggests that the levels of pollution due to discharge and deposition at this site have varied during the recent past.

This homologous series occurs extensively in surface sediments and vegetation originating from these sites. These pollutants can occur as a result of biodegradation of detergent additives [20,21] - $LABSO_3^-$ homologues through desulphonation but are also present, at low levels, as impurities in the $LABSO_3^-$ components. The levels of LABs are in the range of mid μgkg^{-1} to low $mgkg^{-1}$ in surface sediment and low $mgkg^{-1}$ in vegetation. The levels observed are in broad agreement with those reported previously for other estuarine regions [15], 0.2 to 26

Table 6: Concentrations of selected PAH pollutants in a core sediment section from Site B at 11 cm depth.

S.No	Compound	Ions, m/z	$mgkg^{-1}$
1.	Naphthalene	128	0.65
2.	1-methyl[a] naphthalene	142, 141, 115	158
3.	1,1-biphenyl	154	0.33
4.	Acenaphthene	154	0.21
5.	2-ethyl[a] naphthalene	156, 141, 115	1.01
6.	1,2-dimethyl[a] naphthalene	156, 141	0.087
7.	1,8-dimethyl[a] naphthalene	156, 141	0.54
8.	1,4,5-trimethyl[a]	155	0.03
9.	1,4,6-trimethyl[a]	155	0.032
10.	2,3,6-trimethyl[a]	170	0.012
11.	Dibenzofuran	168	0.75
12.	Anthracene/Phenanthrene	178	1.87
13.	Fluoranthene	202	1.7
14.	Pyrene	202	1.4
15.	Triphenylene/Chrysene	228	0.90
16.	benz(e) acenaphthene	252	0.91

[a]alkyl naphthalene isomers referenced by RIs in closest agreement with literature values from reference [12]. PAHs numbered in accordance with order in profile illustrated in Figure 2.
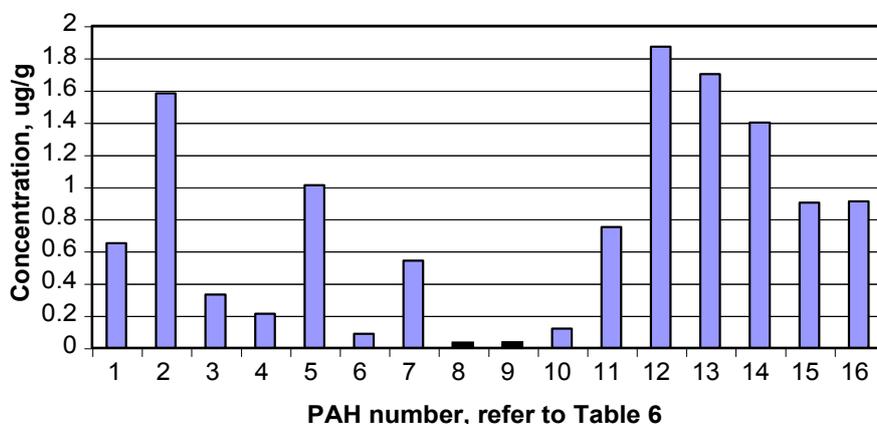

Figure 2: Composition of PAH in core sediment at a depth of 11 cm, Bao Shan, site B; for PAH identity refer to numbering in Table 6.
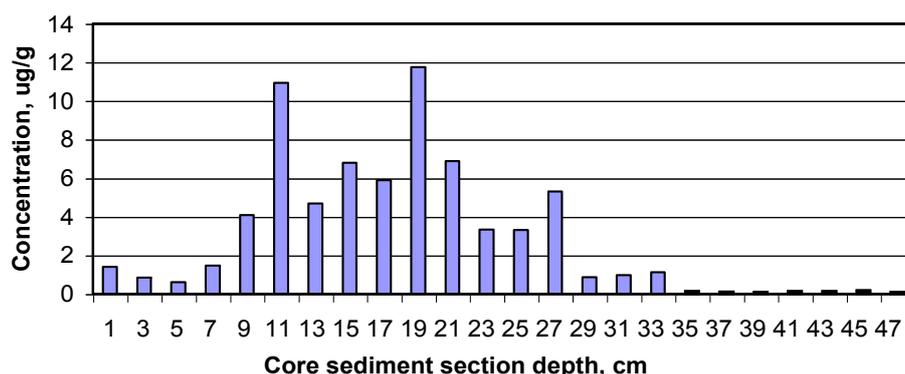

Figure 3: Profile of total PAH concentration in core sediment sections at depths from 1 to 47 cm, Bao Shan, site B.

mgkg^{-1}. The trend in abundance of these LABs correlates with the location - nearness of the site to the mouth of the sewage outlet within the transect of the sampling sites (A1 to D1) of the surface samples taken (analysis of surface sediment from sites B and D exemplify this effect). Four of the LABs that have been at the focus of previous studies [16] are illustrative of this trend. In vegetation, as with core sediment, a wider range of LABs was identified with concentrations approaching the mgkg^{-1} range.

Analogous results have been reported the distribution of LABs in the North Sea [22].

Individual target pollutants: There were isolated incidents of organic pollution involving potentially toxic compounds in selected cores from several sites that were expected to exhibit higher levels of contamination. Both Bao Shan and Wu Song Kou demonstrated these pollutants. Little evidence was found for chlorinated pesticides except in one instance for Bao Shan (1995). The level of contamination for the single pollutants was found to be minor, mid μgkg^{-1} to low mgkg^{-1}. However, Phenyl β-naphthylamine was detected at much enhanced levels in core sediment from Wu Song Kou. The incidence was rather isolated and within ± 2 cm of a depth of 57 cm for which the level was of the order of 100 mgkg^{-1}; the amount reduced to an undetectable level above this depth. This compound that has been used variously as an anti-oxidant and corrosion inhibitor, and, as an additive to rubber, is carcinogenic and would present a hazard if not found only in a hot spot [23,24]. The insecticidal compound -N, N-diethylamide-3-methyl benzamide [25], was detected in sediment from Bao Shan in 1996 in sections 1-13 cm at concentrations of 4-20 mgkg^{-1}.

In surface sediments several specific analytes were detected and showed the same concentration trend with samples across the transect exhibiting a decrease with distance from mouth of the sewage outlet. A particular example of a hazardous pollutant is 2,6-diisopropyl naphthalene (2,6-DIPN [16,26]) that was found in the six intertidal surface sediment samples at concentrations in the range 3 to 11.5 mgkg^{-1}. 2,6-DIPN has been found in fish and river sediment downstream from a waste recycling plant in Japan; river water and sediments in Tokyo Bay; in fish from Green Bay of Fox River system in Wisconsin and in sludge and waste water from a paper mill outside the Fox River area at Oconto Falls, Wisconsin. The toxicity, bioaccumulation and metabolism of 2,6-DIPN have been studied because of its sole use as a dye solvent in carbonless copy paper (Japan and USA) [26] and LD50 (14 day) of 2 gkg^{-1} was demonstrated. Bioaccumulation by a factor of 200 for 5 mgkg^{-1} exposure and metabolic rates of 50% in 56 have been reported.

Other individual organic pollutants found in selected sediments included dibenzofuran and benzophenone.

Other analytes of significance - human waste: Late eluting components which appear to predominate in sediments originating in samples taken from sites adjacent to domestic waste outfalls can be described as a specific group of compounds with sterane-based structures. These components are characterised by m/z, 215, 257, 355 and 370 (M^{+}) with molecular ion species having %RA in the range, 8-10%. The presence of m/z, 215 can be identified with a single double bond function, as reported for β2-sterenes [27,28]. The mass spectral match with factors > 700 (indicating tentative identification and classification) to the data base mass spectra, typical of sterane derivatives with alkyl branched side chains with a mass shift of 2 u from the fully-saturated sterane analogues possessing ions at m/z, 217, 259, 357 and 372.

It is possible that these substances may result from the biological modification of the original substances, hormone-related, biologically active compounds. In support, it has been reported that β2-sterenes can be formed by microbiological reduction and consecutive dehydration of β5-sterols, such as cholesterol and stigmasterol [27].

The general fragmentation to yield m/z, 217 for the steranes and, in this instance, m/z, 215 for the observed analogues can be explained by consideration of the breakdown of the parent sterane/sterene nucleus and derivatives (branched alkyl side chain on C-1 of the cyclopentane, ring D) [29].

The much-simplified profile of components compared to a profile typical of source rock extracts and crude oil [30] together with the mass shift does not support a geochemical origin for these components in the sediments from the sites monitored and from Bao Shan, in particular.

The occurrence of biologically-related molecules in intertidal surface sediments (Bao Shan) are estimated to be in the range of concentrations, 0.1 to 73 mgkg^{-1}, varying across the transect (4 sampling points per site, parallel to the sea, 50 m apart) with the same trend as for LABs. This observation adds weight to the suggestion that these substances are the result of deposition of human waste materials in the vicinity of the sewage outlet. A wider range of analytes of this type are found in surface samples than in core samples which could also be related to oestrogenic and related hormonal substances (17β-oestradiol). There is an interest in the possibility, therefore, that these substances are hormone mimics. The presence of such compounds in water resulting from sewage discharge, and on transfer, in local sediments at concentrations that pose a threat to aquatic organisms and, importantly, fish, makes it imperative that the levels are exhaustively monitored and the effects, such as feminisation, are thoroughly investigated.

Baugh et al. Current Trends Anal Bioanal Chem 2018, 2(1):64-73

ISSN: 2642-4266 | • Page 71 •

Conclusions

It is evident that surface and core sediments, and, vegetation originating from sites in the Yangtze River south coast estuarine region are widely polluted with a range of organics, particularly when receiving waters from outfall sources. Because of the changing nature of the sedimentation the organic pollution is found at a range of depths and has a degree of persistence dependent on the rate of microbial degradation. There is a need for a continuous monitoring programme because of the excessive levels of hormonal-related substances that have the potential to adversely affect the aquatic life, including bottom feeders and fish (Supplementary Text and Supplementary References).

Acknowledgements

References

1. Guzella L, Depaolis A (1994) Polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea. Marine Pollution Bulletin 28: 159-165.

2. Baumard P, Budzinski H, Garrigues P (1998) PAHs in Arcachon Bay, France: Origin and biomonitoring with caged organisms. Marine Pollution Bulletin 36: 577-586.

3. Witt G (1995) Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Marine Pollution Bulletin 31: 237-248.

4. Benlaheen KT, Chaoui A, Budzinski H, et al. (1997) Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. Marine Pollution Bulletin 34: 298-305.

5. Budzinski H, Jones I, Bellocq J, et al. (1997) Evaluation of sediment contamination by polycyclic aromatic hydrocarbon in the Gironde Estuary. Marine Chemistry 58: 85-97.

6. Botella AV, Villanueva SF, Diaz GG, et al. (1998) Polycyclic aromatic hydrocarbons in sediments from Salina Cruz harbour and coastal areas, Oaxaca, Mexico. Marine Pollution Bulletin 36: 544-558.

7. Liu M, Baugh PJ, Hutchinson SM, et al. (2000) Historical record and sources of polycyclic aromatic hydrocarbons in core sediments from the Yangtze Estuary, China. Environmental Pollution 110: 357-365.

8. Ward RM, Liang W (1995) Shanghai water supply and wastewater disposal. The Geog Review 85: 141-156.

9. Min L, Shiyuan X (1998) The Abstracts of the First Asian-Pacific International Symposium on Environmental Geochemistry. Hong Kong Polytechnic University Press, Hong Kong, 52.

10. Min L, Shiyuan X, C Zhenlou (1998) China Environmental Science 18: 284-288.

11. Crompton TR (1999) Determination of Organic Compounds in Soils, Sediments and Sludges. CRC Press, 518.

12. https://www.epa.gov/sites/production/files/2015-12/documents/8275a.pdf

13. (1979) EPA Handbook for Analytical Quality Control in Water and Waste Water Laboratories.

14. Lee ML, Vassilaros DL, White CM, et al. (1979) Anal Chem 48.

15. Elizalde-Gonzalez MP, Hutfliess M, Hedden K (1996) Retention index system, adsorption characteristics, and sructure correlations of polycyclic aromatic hydrocarbons in fuels. J High Resolut Chromatogr 19: 345-352.

16. Peterman PH, Delfino JJ (1990) Identification of isopropylbiphenyl, alkyl diphenylmethanes, diisopropylnaphthalene, linear alkyl benzenes and other polychlorinated biphenyl replacement compounds in effluents, sediments and fish in the fox river system, Wisconsin. Biomedical and Environmental Mass Spectrometry 19: 755-770.

17. Xu S, Tao J, Chen Z, et al. (1997) Oceanologia Et Limnologia Sinica 28: 509-515.

18. Martinez E, Gros M, Lacorte S, et al. (2004) Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediments and mussels. J Chromatogr A 1047: 181-188.

19. Dong CD, Chen CF, Chen CW (2012) Determination of polycyclic aromatic hydrocarbons in industrial harbour sediments by GC-MS. Int J Environ Res Public Health 9: 2175-2188.

20. McEvoy DC, Eckhoff WS, Rapaport RA (1993) Fate of linear alkylbenzene sulfonate in the environment. Environ Toxicol Chem 12: 977-987.

21. Ketesz MA, Kolbener P, Stockinger H, et al. (1994) Desulfonation of linear alkylbenzenesulfonate surfactants and related compounds by bacteria. Appl Environ Microbiol 60: 2296-2303.

22. Raymundo CC, Preston MR (1992) The distribution of linear alkylbenzenes in coastal and estuarine sediments of the western North Sea. Marine Pollution Bulletin 24: 138-146.

23. (1991) Occupational Health Services, Inc. Material Safety Data Sheets (MSDS) for N-phenyl-1napthylamine and N-phenyl-2-naphthylamine.

24. Wang HW, Wang D, Dzeng W (1984) Carcinogenicity of /V-Phenyl-1-naphthylamme and JV-Phenyl-. 2-naphthylamine in Mice. Cancer Res 44: 3098-3100.

25. Qui H, Jun HW, McCall JW (1998) Pharmacokinetics, formulation, and safety of insect repellent N,N-diethyl-3-methylbenzamide. J Am Mosq Control Assoc 14: 12-27.

26. Sturaro A, Parvoli G, Rella R, et al. (1994) Food contamination by diisopropylnaphthalenes from cardboard packages. Int J Food Science and Technology 29: 593-603.

Baugh et al. Current Trends Anal Bioanal Chem 2018, 2(1):64-73

ISSN: 2642-4266 | • Page 72 •

27. Dastillung M, Albrecht P (1977) β2-Sterenes as diagenetic intermediates in sediments. Nature 269: 678-679.

28. Louati A, Elleuch B, Kallel M, et al. (2001) Hydrocarbon contamination of coastal sediments from the Sfax area (Tunisia), Mediterranean Sea. Marine Pollution Bulletin 42: 445-452.

29. Budzikiewicz H, Djerassi C, Williams DH (1967) Mass Spectrometry of Organic Compounds. In: Gordon & Breach, California, 690.

30. Harriman GE (1993) The role of gas chromatography in petroleum exploration. In: Gas Chromatography - A practical approach. PJ Baugh, Oxford University Press, Oxford, 331-358.

SCHOLARS.DIRECT