pling programme, the calculated dilution suggested that even a substantial bulk water release was highly unlikely to pose a significant threat to the surrounding environment. However, if the results had suggested much higher levels of toxicity (precisely how toxic would have been determined by producing a median lethal effect, LC50, value from a dilution series) this would have alerted the salvage team to take specific precautions to minimise the release from the holds into the environment and may have informed alternative control operations such as the removal of the hold water to a tanker or via a controlled release. It is in this way that this approach could play an important part in understanding the potential effects of shipping accidents and in informing the salvage and mitigation activities. In the context of the MSC Napoli incident the use of this approach provided important assurance to the environment group, conservationists and the general public that the release of the hold contents (58,000 tonnes of water was pumped overboard during the refloating of the vessel) was unlikely to result in significant detriment to the surrounding biota.

The opportunity to deploy a toxicity test method to the assessment of cargo-mediated hazard assessment in a real incident has allowed the value of such an approach to be confirmed. This approach could be applied to the hazard assessment of water within any enclosed or semi-enclosed vessel in the event of an incident at sea provided that access is available for sampling. This clearly has applications to

shipping accidents but may also be applied to other scenarios. It is recommended that the approach be developed into a more standardised methodology for deployment at short notice in emergency response situations. A range of other short-term bioassays or screening tests (e.g. to assess endocrine disruption, genotoxicity etc.) could be used in this context dependent on the perceived nature of the hazard. For optimum value the method should be used in conjunction with appropriate hydrodynamic models to assess dilution factors in the vicinity of the incident.

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Chemical speciation of 12 metals in surface sediments from the northern South China Sea under natural grain size

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Metals exist in several different forms and are associated with a range of components in soils and sediments. The particular behavior of metals in the environment is determined not only by their total concentration but also by their specific physicochemical forms (Bernhard et al., 1986). In an aquatic environment, the chemical form of a metal determines the biological availability and chemical

reactivity towards other components of the system (Bubb and Lester, 1991).

The northern South China Sea (NSCS) records various substantial anthropogenic influences from the Pearl River Delta economic region. Anthropogenic influences on the composition of non-aromatic hydrocarbons in surface sediments of the NSCS outer continental shelf have been identified (Gao et al., 2007). The concentration, chemical speciation and transport of sedimentary metals, mainly confined to Co, Cu, Cr, Ni, Pb and Zn, from the Pearl River have been extensively studied in recent years (e.g. Li et al., 2000,

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2001; Liu et al., 2003; Fang et al., 2005; Ip et al., 2007). Most of these studies, however, were limited to the Pearl River Estuary and its adjacent coastal regions. Few researchers have used sequential extraction technique to determine the chemical speciation of metals in sediments of the NSCS off the Pearl River Estuary. The aim of this study is to determine both the concentrations of 12 metallic elements in surface sediments of the NSCS continental shelf and shelf slope, including Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sc, Sr, U and Zn, and the chemical forms in which they occur by the BCR (Community Bureau of Reference, now superseded by the Standards, Measurement and Testing Programme of the European Community) sequential extraction procedure.

Surface sediments were collected from four sites in the NSCS off the Pearl River Estuary using a box grab sampler in September 2005 (Fig. 1). Sites E1, E2 and E3 are located at the continental shelf, while site E4 is located at the shelf slope. The geographic coordinates and water depth of each sampling site are shown in Table 1. Undisturbed top 5 cm sediments were sampled and placed in acid-rinsed polypropylene bags using a plastic spatula. Only one sample was collected from each sampling station. The samples were stored at ~4 °C in the dark until further analysis. The sample granulometry was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following 3 grain size groups were determined: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand). The results indicate that sediment of site E4 is mainly composed of silt, whereas those of the other three sites are mainly composed of sand (Table 1).
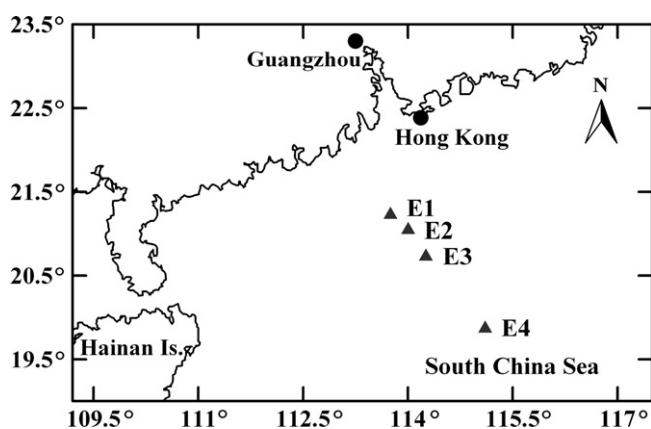

Fig. 1. Location of sampling sites in the northern South China Sea.

Table 1
The geographic coordinates and water depth of each sampling site and the grain size composition of the sediments sampled

Site	Longitude (E)	Latitude (N)	Depth (m)	Clay (%)	Silt (%)	Sand (%)
E1	115°6.314′	19°53.468′	62	8.95	29.42	61.63
E2	114°15.352′	20°45.034′	74	9.92	25.90	64.18
E3	114°0.217′	21°4.084′	79	0.11	2.52	97.37
E4	113°44.982′	21°15.044′	1182	27.62	68.70	3.68

In general, sediment samples were dried and ground before extraction (e.g. Tokalioğlu et al., 2000; Gismera et al., 2004). Although the dry samples are easier to treat than the wet ones, it has been reported that sample drying could alter the solid phase distribution of metals (Rapin et al., 1986; Davidson et al., 1999; Hjorth, 2004). Furthermore, the metal concentrations in aquatic sediments are highly dependent on the sediment grain size (Horowitz and Elrick, 1988; Howari and Banat, 2001), and a trituration treatment could potentially alter the extractability of metals from soil samples (e.g. Gilliam and Richter, 1988). In this work, to reduce the errors, wet and unground samples were used for the sequential extraction procedure. The homogenized samples were sub-sampled and put into 50 ml polypropylene centrifuge tubes and weighed to obtain the wet weight corresponding to approximately 0.5 g dry weight based on water content measurements. The water content of the sediment was determined gravimetrically by comparing the weight difference before and after heating an aliquot of the sample to 105 °C overnight.

The BCR 3-step sequential extraction procedure modified by Rauret et al. (1999) was used to obtain the information about the non-residual speciation of metals. The fourth step involving digestion of residue from the third step with aqua regia was introduced to obtain an indication of the concentrations of these elements associated with the residual components of sediment matrix (Rauret et al., 1999). The total digestion of sediments was performed by the same method used in the fourth step. The total concentrations of metals in the sediments were estimated by summing up the results of the four steps, and account for 82–108% of the values from the total digestion experiment, which is within the range of other reports (e.g. Martin et al., 1998; Li et al., 2001; Yuan et al., 2004).

The sequential extraction protocol used, along with the sediment fractions from which metals are released, is summarized in Table 2 (Rauret et al., 1999). Between the extraction steps, solid/liquid separation was achieved by centrifuging at 4000 rpm for 20 min, the resulting supernatant being decanted into polyethylene bottles and stored at 4 °C until analysis. Residues were then washed with 10 ml de-ionized water (Milli-Q), shaken for 15 min, and centrifuged at 4000 rpm for 20 min, the supernatant being discarded. The sequential extraction procedure was carried out with no interruption once started (Ajay and van Loon, 1989). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500) was applied in this work for the determination of Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sc, Sr, U and Zn. The concentrations of Al were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin–Elmer Optima 3300 DV) to calculate the enrichment factor for each element. The Chinese national geostandard samples of GSS-1 and GSS-8 were used to control the analytical quality. The results are consistent with the reference values, and the differences are all within 10% (most are within 5%). All plasticware and glassware were pre-cleaned by soaking in 10% HNO_3 (v/v) for

Table 2
Summary of the BCR sequential extraction protocol

Step	Fraction	Components extracted	Extraction reagent	Extraction method
I	Fraction 1, acid soluble	Exchangeable and bound to carbonates	20 ml 0.11 mol l^{-1} HOAc	Shaking at 22 ± 5 °C for 16 h
II	Fraction 2, reducible	Bound to Fe/Mn oxides	20 ml 0.5 mol l^{-1} NH$_2$OH·HCl (adjusted to pH 1.5 with HNO$_3$)	Shaking at 22 ± 5 °C for 16 h
IV	Fraction 3, oxidizable	Bound to organic matter and sulphides	5 ml 8.8 mol l^{-1} H$_2$O$_2$ (adjusted to pH 2.0 with HNO$_3$)/another 5 ml 8.8 mol l^{-1} H$_2$O$_2$ (adjusted to pH 2.0 with HNO$_3$)/25 ml 1 mol l^{-1} NH$_4$OAc (adjusted to pH 2.0 with HNO$_3$)	Digesting at room temperature for 1 h with occasional manual shaking, then cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to a few milliliters/cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to near dryness/shaking at 22 ± 5 °C for 16 h
V	Fraction 4, residual	Metals within lithogenic minerals	Aqua regia	

For each sample, the wet weight corresponding to approximately 0.5 g dry weight based on water content measurements was used.

at least 2 days, followed by soaking and rinsing with de-ionized water. All chemicals used in the experiment were analytical-reagent grade. Blank determinations were carried out for each set of analysis using the same reagents. All data were corrected for dry weight of the sample.

The concentrations of metals in NSCS surface sediments from each extraction step and their total concentrations are shown in Table 3. The total metal concentrations are found to vary greatly with sites. The maximum values of metals are all recorded at site E4 with no exception. It has been reported that the concentrations of Cd, Cu, Pb and Zn in sediments of the South China Sea shelf slope are generally higher than those in sediments of the coastal area of the Sea (Zhang and Du, 2005). The Cd, Cu, Pb and Zn contents recorded at site E4 are within the range of their values in sediments of the South China Sea shelf slope. The metal concentrations decreased spatially from site E1 to E3 except for Cd, showing a clue that their spatial distributions may be influenced by Pearl River discharge. The total contents of Cu, Ni, Pb and Zn at sites E1 to E3 are lower than the background values of the marine and estuary sediments in Hong Kong. Combined with the speciation and enrichment factor data, which will be discussed below, it is likely that the influence of Pearl River discharge on the sedimentary metals of sites E1 to E3 is little. For most of the 12 metals, their total contents at sites E1 to E3 are lower than at the upper continental crust, while their total contents at site E4 are comparable to those at the upper continental crust (Table 3).

Among the four studied sites, site E4 is the only one where the concentrations of Co, Cu, Ni and Zn in its surface sediments are comparable to those in surface sediments at the Pearl River Estuary, although it is the farthest site from the Pearl River Estuary (Table 3). Their contents at the other three sites are much lower than those at the Pearl River Estuary. Former research indicates that grain size, as well as heavy minerals, is an important factor that controls the distribution of chemical elements in the Pearl River Estuary (Zhou et al., 2004). Granulometry results indicated that sediment at site E4 is much finer than at the other three sites. This is likely being a reason that metals at site E4 are much higher than at the other sites.

The speciation data show that the studied metals in the residual fraction are much higher than those in the non-residual fractions, except for Cd, Mn and Sr (Fig. 2), indicating that they are mainly from crustal materials. The concentrations of Sc in the non-residual fractions at all sampling sites account for <5% of its total concentrations. The concentrations of Ba in the non-residual fractions at sites E1 to E3, and the concentrations of Cu in the non-residual fractions at sites E1 and E2 account for <5% of their respective total concentrations too. The percentages of the non-residual fractions of Co, Mo, Ni, Pb, U and Zn, change within the wide range of 7–45% of their total concentrations depending on location (Fig. 2).

The predominant proportions of Ba, Mo and Ni present in the residual fraction are in agreement with the results of some other studies (Martin et al., 1998; Mester et al., 1998; Kryc et al., 2003; Yuan et al., 2004). The speciation pattern of Cd is found to be highly variable with sampling sites (Fig. 2), which is similar to the research carried out in the East China Sea (Yuan et al., 2004). The percentage of Cd in the oxidizable fraction is similar at the four sampling sites, while it is found to vary greatly with sites in the other fractions. The speciation patterns of Co and Zn are similar to those obtained in the sediments of East China Sea (Yuan et al., 2004).

A number of previous studies on different kinds of sediments show that Cu are mainly associated with the oxidizable phase, occurring as organically complexed metal species (e.g. Pardo et al., 1993; Marin et al., 1997; Fytianos and Lourantou, 2004). This is because Cu shows high affinity with humic substances, which are a fraction of natural organic matter chemically active in complexing such metals

Table 3
Metal contents extracted from each step of the BCR sequential extraction procedure and the sum of contents from all steps

	Site	Ba	Cd	Co	Cu	Mn	Mo	Ni	Pb	Sc	Sr	U	Zn
Fraction 1	E1	1.39	0.005	0.460	0.114	172	ND[a]	1.67	1.17	0.056	210	0.120	0.76
	E2	2.40	0.018	0.248	0.066	114	0.002	1.53	0.52	0.066	193	0.039	0.25
	E3	1.35	0.012	0.168	0.140	66.9	0.015	1.94	0.05	0.090	394	0.077	0.36
	E4	11.2	0.108	0.345	0.333	199	0.076	3.93	0.10	0.091	410	0.177	1.73
Fraction 2	E1	1.43	0.008	1.70	ND	48.9	0.002	1.71	6.82	ND	8.57	0.090	7.59
	E2	1.19	0.003	0.951	ND	26.2	0.004	1.21	3.43	ND	4.59	0.039	4.66
	E3	1.79	0.013	0.406	ND	29.9	0.014	0.87	1.18	ND	71.1	0.020	1.63
	E4	91.1	0.126	1.29	ND	195	0.011	4.02	0.29	ND	77.8	0.001	5.18
Fraction 3	E1	2.48	0.004	0.840	0.079	13.9	0.074	1.93	0.54	0.071	0.87	0.242	4.07
	E2	2.63	0.004	0.697	0.002	9.76	0.056	1.40	0.33	0.058	0.41	0.093	5.08
	E3	3.08	0.005	0.639	0.141	9.67	0.066	1.50	0.62	0.066	1.82	0.127	6.14
	E4	108	0.037	1.50	4.59	35.4	0.171	7.25	2.69	0.101	12.6	0.316	11.3
Fraction 4	E1	293	0.027	5.01	8.10	115	1.01	13.8	12.5	6.80	45.0	1.29	49.3
	E2	259	0.015	3.70	6.00	104	0.550	9.30	12.5	4.80	40.1	1.25	33.6
	E3	149	0.016	2.10	3.40	68.0	0.512	5.40	9.70	3.10	25.0	1.02	20.2
	E4	391	0.037	12.8	33.5	279	0.841	33.0	19.3	14.7	75.3	1.51	128
Sum	E1	298	0.044	8.01	8.29	350	1.09	19.1	21.0	6.93	264	1.74	61.7
	E2	265	0.040	5.60	6.07	254	0.612	13.4	16.8	4.92	238	1.42	43.6
	E3	155	0.047	3.31	3.68	174	0.607	9.71	11.6	3.26	492	1.24	28.3
	E4	601	0.308	15.9	38.4	708	1.10	48.2	22.4	14.9	576	2.00	146
	UCC[b]	550	0.098	10	25	600	1.5	20	20	11	350	2.8	71
	PRE[c]			16.3	40.9			33	59.5				114.5
	PRE[d]			40.2	46.2			41.7	59.3				150
	Marine BV[e]				15			25	50				94
	Estuary BV[f]				10			15	29				70

The corresponding values of the metals in the upper continental crust and the sediments from the area around the Pearl River Estuary were also listed.
Content unit is µg g⁻¹ dry sediment for all elements.

[a] ND means not detected.
[b] Average concentrations of the upper continental crust (Taylor and McLennan, 1995).
[c] Average concentrations of the surface 0–5 cm sediments in Pearl River Estuary (Li et al., 2000).
[d] Average concentrations of the surface 0–10 cm sediments in Pearl River Estuary (Zhou et al., 2004).
[e] Background values of the marine sediments in Hong Kong (Tanner et al., 2000).
[f] Background values of the estuary sediments in Hong Kong (Tanner et al., 2000).

(Pempkowiak et al., 1999). In this study, 87–99% of total Cu is found in the residual fraction (Fig. 2), indicating that it is mainly of lithogenic origin. This coincides with the researches carried out in the Pearl River Estuary and East China Sea (Liu et al., 2003; Yuan et al., 2004).

As observed by many other researchers (e.g. Tack and Verloo, 1995; Yuan et al., 2004; Naimo et al., 2005), for all the samples studied in this work, a large proportion of total Mn, accounting for 28–49% of its total content, is found in the acid soluble fraction (Fig. 2). The spatial variation of the percentages of Mn in the oxidizable and residual fractions between sites is smaller than that in the other two fractions; the percentage of Mn in the acid soluble fraction decreases apparently from site E1 to E4.

At sites E1 to E3, the reducible Pb is more abundant than the other two non-residual fractions of Pb (Fig. 2). The fact that Pb can form stable complexes with Fe and Mn dioxide (Ramos et al., 1994) may be the reason for this. The reducible Pb predominating in the non-residual fractions has been reported by many researchers (e.g. Fernandes, 1997; Li et al., 2001; Ip et al., 2007).

For Sr, 71–81% of its total concentration is associated with the acid soluble fraction, and only 0.2–2% of its total concentrations is associated with the oxidizable fraction (Fig. 2). The acid soluble fraction represents the total of the ion-exchangeable and carbonate components of the sediment matter. Xu and Marcantonio (2004) reported that ~16% of Sr in the exchangeable and carbonate components can be released by de-ionized water for a particulate sample collected from the Mississippi River mixing zone. Their work provides a minimum baseline for the exchangeable fraction since seawater has higher ionic strength than de-ionized water, and then an even higher proportion of exchangeable Sr is expected.

The study on some river sediments indicates that a majority of total U is associated with the non-residual fractions, owing to the anthropogenic influences (Martínez-Aguirre et al., 1995). More than 70% of the total U in NSCS surface sediments is present in the residual fraction (Fig. 2), indicating that it is mainly from rock and soil weathering.

The enrichment factor (EF) for each element was calculated to evaluate anthropogenic influences on the studied metals in NSCS surface sediments using the following formula (Feng et al., 2004; Selvaraj et al., 2004):

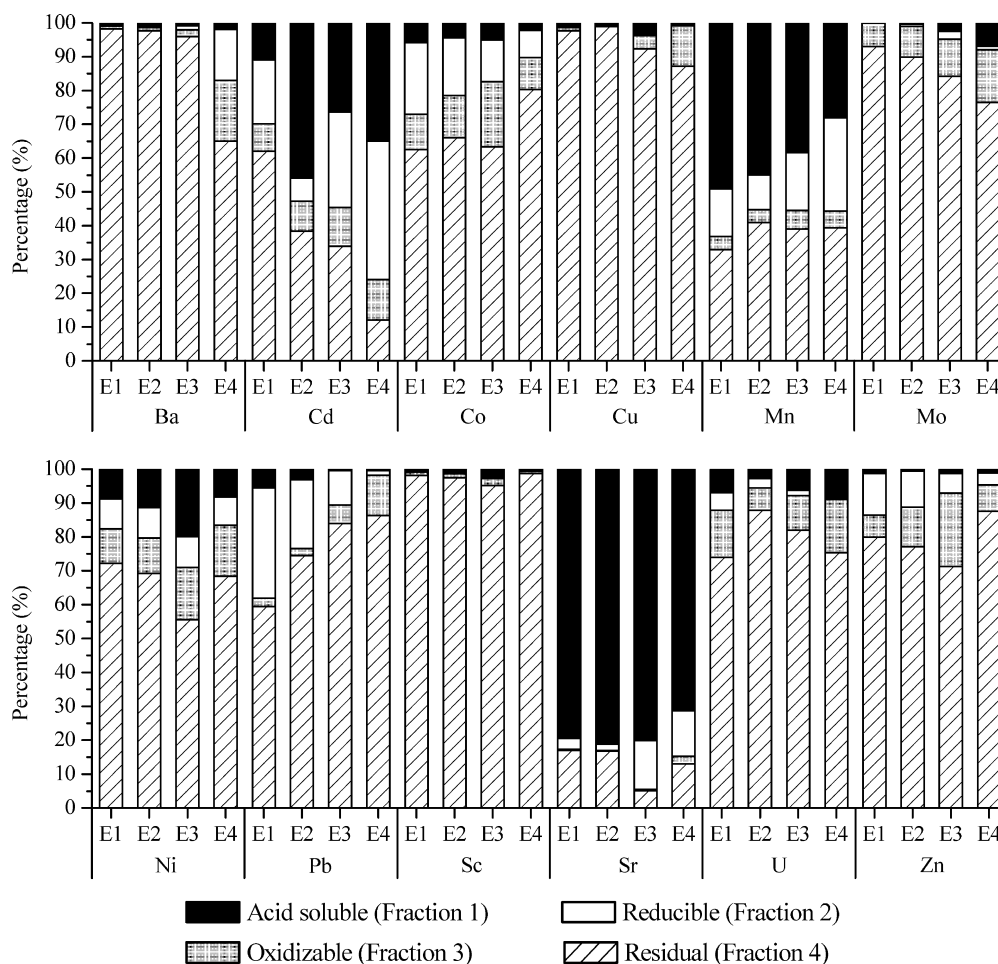$$EF = (C_x/C_{Al})_S/(C_x/C_{Al})_{UCC}$$

Fig. 2. The percentage of metals extracted in each step of the BCR sequential extraction procedure.

Table 4
The EF values of 12 studied metals in the northern South China Sea surface sediments

Site	Ba	Cd	Co	Cu	Mn	Mo	Ni	Pb	Sc	Sr	U	Zn
E1	0.86	0.72	1.27	0.54	0.93	1.15	1.52	1.67	1.00	1.20	0.99	1.38
E2	1.02	0.89	1.22	0.53	0.92	0.89	1.46	1.83	0.98	1.48	1.11	1.34
E3	0.98	1.65	1.15	0.51	1.01	1.41	1.69	2.01	1.03	4.88	1.54	1.38
E4	1.05	3.01	1.52	1.47	1.13	0.70	2.31	1.07	1.30	1.58	0.68	1.97

where C_x and C_{Al} denote the concentrations of elements x and Al in the samples of interest (S) and the upper continental crust (UCC) (Taylor and McLennan, 1995).

Generally, an EF value of about 1 suggests that a given metal may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). Nevertheless, a slight positive deviation of EF value from unity may not arise from anthropogenic activities, for the natural difference in elemental composition between a pristine sediment and the reference Earth's crust used in EF calculation could also cause it. An EF value of >1.5 suggests that a significant portion of a given metal is delivered from non-crustal materials, or non-natural weathering processes, and then anthropogenic sources become an important contributor (Feng et al., 2004). The highest EFs in this study

are recorded at site E4 except for Mo, Pb, Sr and U, and 5 of the 12 metals, including Cd, Co, Ni, Sr and Zn, have an EF of >1.5 at this site suggesting possible sediment contamination due to anthropogenic activities (Table 4). At sites E1 to E3, the EFs of Ba, Co, Cu, Mn, Mo, Sc and Zn are all <1.5; the EFs of Cd, Sr and U are >1.5 at site E3; the EFs of Ni are >1.5 at sites E1 and E3; the EF of Pb is >1.5 at all the three sites (Table 4). The EFs of Cd, Pb, Sr and U increase from site E1 to E3; the EFs of Co and Cu decrease from site E1 to E3 (Table 4).

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PFOS and PFOA in the livers of harbour porpoises (*Phocoena phocoena*) stranded or bycaught around the UK

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In 2001, Giesy and Kannan reported on the global distribution of perfluorooctane sulphonate (PFOS), a fluorinated organic contaminant, in wildlife. PFOS was determined in tissues of fish, birds, amphibians, and aquatic mammals (including seals and dolphins). Their study demonstrated that PFOS was widely distributed on a global scale and that it can be persistent and bioaccumulative in various food chains. PFOS does not accumulate in lipid-rich tissues such as blubber, but rather binds to specific proteins in liver, kidney and blood plasma (Van de Vijver et al., 2003). Temporal trend studies have shown increases in PFOS concentrations in wildlife, particularly during the 1990s (Houde et al., 2006a). Little information was available on possible toxic effects of PFOS in wildlife, though they may adversely affect cell membranes and intercellular communication and can cause developmental and neuroendocrine anomalies in rodents (Houde et al., 2006b). Subsequently, a number of other studies of perfluorinated organic acids in the environment have been conducted.

Within the OSPAR Hazardous Substances Strategy, PFOS and its salts are included in their list of chemicals for priority action (OSPAR, 2007). As part of the justification for this inclusion, a background document was prepared (OSPAR, 2006). This noted that PFOS and related compounds are used in a wide range of applications and products, including providing water and oil resistance to textiles, carpets and papers; use in the metal plating, photographic and semiconductor industries, in hydraulic fluids of aircraft, in fire fighting foams, in flame retardants, as active ingredients in pesticides and insecticides, in industrial and household cleaning products, in medical applications and as mining and oil surfactants. In 2000, the total global production of PFOS by the US 3M Corporation was estimated at ca. 3700 tonnes. 3M phased out production from 2001, but production continued in Germany, Switzerland, Russia and Japan, although no volume data are available (OSPAR, 2006). Given the wide range of uses, environmental sources are manifold and widespread. PFOS-related substances have neither been identified as priority substances under the EU Water Framework Directive nor listed in Annex 1 of the EU Dangerous Substances Directive, and are also not regarded as POPs (Persistent Organic Pollutants) within the Stockholm Convention to date. So far, no EU measures exist to restrict the production, marketing and use of PFOS, although the European Commission still has this under consideration (OSPAR, 2006).

OSPAR's aim is that, for synthetic chemicals such as PFOS, effective controls should ensure that future environmental concentrations fall to zero, or close to zero. This requires that environmental concentrations be determined to provide a baseline from which such reductions can be observed. Marine mammals, as top predators, can accumulate high concentrations of persistent and bioaccumulative organic contaminants, and so can act as effective sentinel organisms for monitoring purposes (Yamashita et al., 2005). In this study, we determined concentrations of PFOS and perfluorooctanoic acid (PFOA) in the livers of harbour porpoises stranded or bycaught around the UK in 1992–2003 (see Fig. 1 for locations).

The porpoises sampled were collected within the marine mammal stranding programme funded by the UK government. Animals which are found stranded or are bycaught in fishing operations and are classified as freshly dead or only slightly decomposed are taken for post-mortem study

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