Available online at www.sciencedirect.com
SCIENCE DIRECT®
Marine Pollution Bulletin 48 (2004) 30–43
MARINE POLLUTION BULLETIN
www.elsevier.com/locate/marpolbul

Organochlorinated compounds in Caspian Sea sediments

Stephen de Mora [a,*], Jean-Pierre Villeneuve [a], Mohammad Reza Sheikholeslami [b], Chantal Cattini [a], Imma Tolosa [a]

[a] *Marine Environment Laboratory, International Atomic Energy Agency, 4 quai Antoine 1er, B.P.800, MC 98012 Principality of Monaco, Monaco*

[b] *Theme for Effective Regional Assessment of Contaminant Levels (ERACL), Department of the Environment (DOE), 187 Nejatollahi Ave, P.O. Box 15875-5181 Tehran, Iran*

Abstract

Several organochlorinated contaminants, including numerous pesticides, were determined in coastal sediments from the Caspian Sea. The most important contaminants were p,p'-DDT (up to 7400 pg g^{-1}) and its breakdown products, p,p'-DDD (up to 3400 pg g^{-1}) and p,p'-DDE (up to 1300 pg g^{-1}). Although the contamination was most severe in Azerbaijan, the sediment concentrations and percentage distribution of the three DDT-related compounds indicated that such contamination constitutes a contemporary and ubiquitous problem in the Caspian Sea. Lindane represented the second most significant contaminant, particularly in the Russian Federation, with concentrations up to 609 pg g^{-1}. The concentrations of HCB and other chlorinated pesticides (*cis*- and *trans*-chlordane, methoxychlor, heptachlor, heptachlor epoxide, aldrin, endrin, and endosulfans) were lower and not generally of concern, but the pesticides did demonstrate markedly different distributions reflecting differing agricultural usage in the region. The concentrations of Σ PCBs were also quite low and ranged from 0.03 to 6.4 ng g^{-1}, with the highest amounts in the Russian Federation and Azerbaijan.

Keywords: Caspian Sea; Sediments; Pollution; Chlorinated hydrocarbons; Pesticides; PCBs

1. Introduction

The Caspian Sea is a unique system straddling several climate zones from continental to Mediterranean due to its north–south orientation. Surrounded by the five littoral states of Azerbaijan, Federation of Russia, Islamic Republic of Iran, Kazakhstan, and Turkmenistan, it is the largest inland body of water in the world (Kosarev and Yablonskaya, 1994). Biologically the Caspian Sea is a special region, with endemism reaching 80% at the species level (Dumont, 1998). However, the biodiversity is relatively low, with the total number of species about 40% of that found in the Black Sea (Karpinsky, 1992).

As a land-locked system, pollutant discharges into the Caspian Sea remain trapped within the basin. Offshore oil production and land-based sources, notably the Volga River, are considered to be the main sources of pollution (Karpinsky, 1992). Of the 130 rivers emptying into the Caspian Sea, the Volga River contributes ~80% of the annual flow. The Kura and Ural Rivers contribute 6% and 5%, respectively, and the remainder of the inflow comes mainly from the numerous rivers in Russia and Iran. The sea level, now ~27 m below the level of the world oceans, increased by about 1.5 m between 1977 and 1995. Pollution was consequently caused by the flooding of oil fields, agricultural lands and toxic waste sites (Dumont, 1995, 1998).

Organochlorinated compounds have seen widespread use, with both industrial and agricultural sources contributing significant amounts to the environment. Owing to their toxicity, they can threaten both the sustainable use of bioresources and public health. A number of studies of organochlorinated compounds in the Caspian Sea has been undertaken, but mostly with respect to the biota. DDT was measured in sturgeon muscle and eggs from the South Caspian Sea, at concentrations of 3.7 and 3.2 μg g^{-1}, respectively (Södergren et al., 1978). In

* Corresponding author. Tel.: +377-97-97-72-72; fax: +377-97-97-72-76.
E-mail address: s.de_mora@iaea.org (S. de Mora).

0025-326X/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2003.10.001

this study, hexachlorobenzene (HCB) and lindane were detected, but not polychlorobiphenyls (PCBs). Another study of organochlorinated compounds in sturgeon from the Iranian sector of the Caspian Sea found notable contamination with respect to DDT and its breakdown metabolites (Ballschmiter et al., 1983). Significant contamination of hexachlorocyclohexanes (HCHs), HCB, and polychloroterpenes was also noted, but levels of PCBs were considered low. A recent study in the northeastern Caspian Sea found measurable amounts of HCHs, DDE and DDT in roach, goby and sturgeon, but levels of PCBs were below the unspecified detection limit (Moore et al., 2003). Like sturgeon, seals from the Iranian sector were contaminated with respect to DDT and its breakdown products, together with β-HCH (Vetter et al., 1995). Chlordanes, toxaphene and PCBs were found only at low levels. Recent studies following the massive mortality of seals have focussed on mammals from the Russian sector of the Caspian Sea (Hall et al., 1999; Kajiwara et al., 2002; Watanabe et al., 1999). The findings provide evidence of widespread contamination of DDTs and HCHs in the Caspian Sea. The content of PCBs was considered much less of a problem.

In contrast to the biological studies, few other environmental compartments have received attention. Some rivers (Terek, Kuma, Volga, and Ural) discharging into the Caspian Sea were included in a nation-wide assessment of fluxes of organochlorinated pesticides in Russian rivers (Zhulidov et al., 2000). The Volga River was the most important source of p,p'-DDT, p,p'-DDE, α-HCH and γ-HCH. However, the flux of γ-HCH from the Terek River was comparable, despite its much smaller size, thereby indicating the importance of agricultural activity in the catchment region. Noting that many of these compounds are persistent in marine systems, the sediments provide a reliable means to assess contamination. One study, based on only 7 congeners, found that Σ PCBs were below the detection limit (i.e. $<0.04\ \mu g\ g^{-1}$) in sediments of the Volga delta (Winkels et al., 1998). Measurable levels of DDT, DDE, α-HCH and β-HCH have recently been reported in 5 sediment samples from the northeastern Caspian Sea (Moore et al., 2003).

This paper presents the first comprehensive survey of several organochlorinated compounds in the sediments of the Caspian Sea. Sediment quality in the coastal zone was interpreted on the basis of 103 samples collected in all littoral states, although only 2 samples were obtained in Turkmenistan, from October 2000 to September 2001. A wide range of organochlorinated compounds, some not previously reported for the Caspian Sea, was determined for pollution assessment and to facilitate interpretation on the origins of the contaminants. Concurrent studies were conducted on metals (de Mora et al., 2003) and petroleum hydrocarbons (Tolosa et al., 2003).

2. Methods

2.1. Sample collection

Details of sampling (de Mora et al., 2004) and station locations (Fig. 1 in Tolosa et al., 2003) have been previously described. Coastal sediments from the Caspian Sea were collected using a Van Veen grab. Sediment from the surface (~4 cm) was sub-sampled and stored in cleaned aluminium containers. All materials were frozen (−18 °C) immediately and kept frozen for transport to the laboratory. The 21 samples from the Russian sector were analysed at the Russian laboratory "Typhoon" Center for Environmental Chemistry. All other samples were analysed at the International Atomic Energy Agency–Marine Environmental Studies Laboratory in Monaco. The samples were analysed for several organochlorinated substances: PCBs, HCHs, HCB, DDTs, endosulfans, and cyclodienes, including chlordanes. The grain size distribution, total organic carbon (TOC), carbonate content, several metals and petroleum hydrocarbons were also analysed (de Mora et al., 2004; Tolosa et al., 2003).

2.2. Analyses

Following freeze-drying, samples were sieved through vibrating stainless steel sieves with mesh size of 250 μm. Sieved sediments were homogenised prior to extraction. A series of internal standards comprising PCB29, PCB198, ε-HCH and α-endosulfan D_4 was added to the sediments for quantifying the overall recovery of the organochlorine fractions. Samples were Soxhlet extracted for 8 h with a 250 ml mixture of hexane/methylene chloride (1:1, v/v). Sulphur was removed using activated elemental copper. Extractable organic matter (EOM) was determined by evaporating a small measured volume of this extract on the pan of an electrobalance.

The extracts were then separated into two aliquots: 1/3 for hydrocarbons and sterols, and 2/3 for chlorinated hydrocarbon analyses. The extract was passed through a Florisil (18.5 g) column, which had been activated for 12 h at 130 °C and partially deactivated with 0.5% water. From this column, three fractions were collected: first fraction with 65 ml of hexane (containing PCBs, p,p' and o,p'-DDE and some other pesticides such as HCB, aldrin, heptachlor, DDMU); second fraction with 45 ml of hexane/methylene chloride (70:30) (containing the DDTs, DDDs, most of the toxaphene and some pesticides such as HCH isomers and chlordane components) and then a third fraction with 55 ml of methylene chloride (containing mainly dieldrin, endrin and endosulfan components).

Organochlorinated compounds were determined by gas chromatography using an electron capture detector

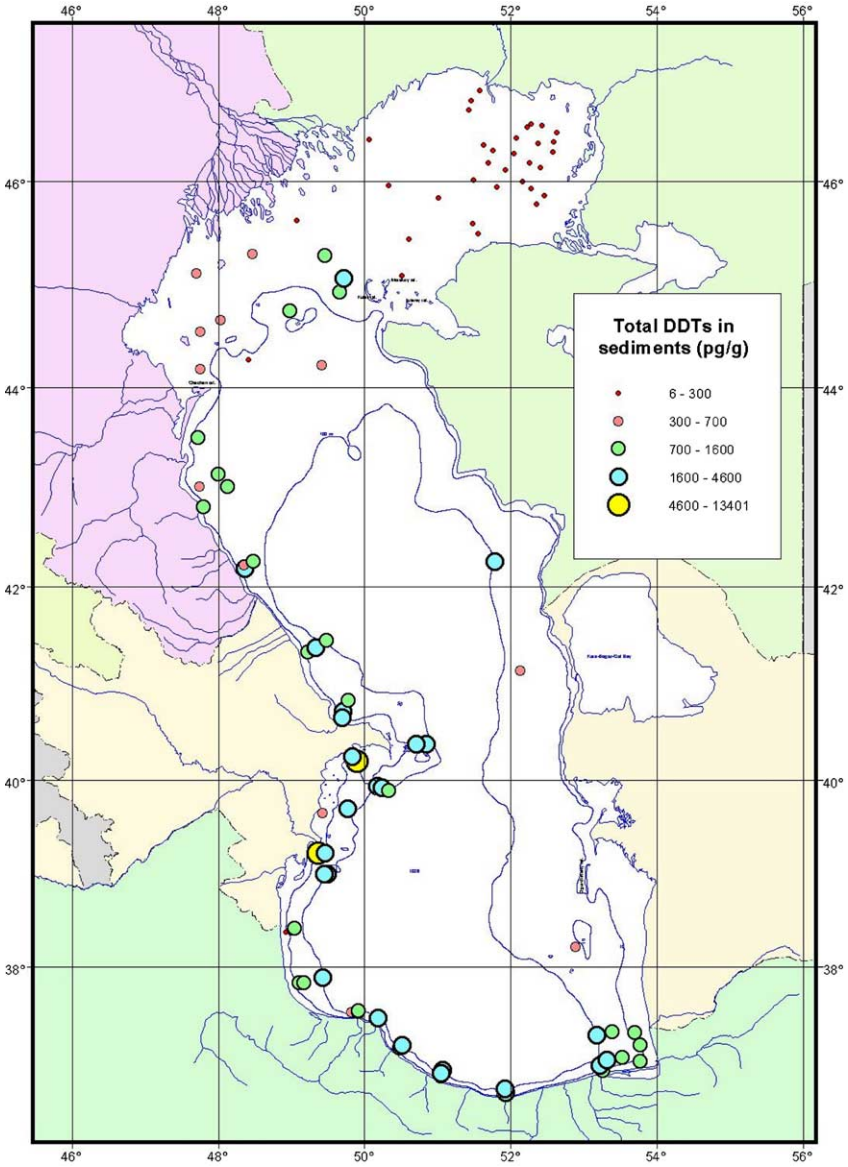

Fig. 1. Σ DDTs (pg g^{-1} dry wt) in coastal sediment from the Caspian Sea.

(Hewlett Packard HP6890 GC-ECD). A splitless injection mode was used. The injector and detector temperatures were maintained at 250 and 300 °C, respectively. For Fractions 1 and 3, the column was a HP-5 (cross-linked 5% PhMe Silicone) 30 m × 0.25 mm i.d. × 0.25 μm film thickness. The flow rate of the carrier gas, helium, was 1.0 ml min^{-1}. The oven temperature programme was 70 °C for 2 min, 70–260 °C at 3 °C min^{-1}, and then 260 °C for 20 min. For Fractions 2 and 3 (Fraction 3 was injected on both columns in order to confirm the quantification of endrin and dieldrin), the column was a HP-5 (cross-linked 5% PhMe Silicone) 20 m × 0.10 mm i.d. × 0.40 μm film thickness. The flow rate of the carrier gas, helium, was 0.4 ml min^{-1}. The oven temperature programme was 100 °C for 0.5 min, 100–140 °C at 9 °C min^{-1}, 140 °C for 0.5 min, 140–250 °C at 2 °C min^{-1}, 250 °C for 0.5 min, 250–300 °C at 12 °C min^{-1}, and finally 300 °C for 15 min.

Quantification of 28 PCB congeners (IUPAC Nos: 2Cl, dichlorophenyls 8; 3Cl, trichlorobiphenyls: 18, 28(+31); 4Cl, tetrachlorobiphenyls 44, 52; 5Cl, pentachlorobiphenyls 95(+66, 4Cl), 101, 105, 110(+77, 4Cl), 118, 126; 6Cl, hexachlorobiphenyls 128, 138, 149, 153, 156, 169; 7Cl, heptachlorobiphenyls 170, 180, 183, 187, 189; 8Cl, octachlorobiphenyl 195; 9Cl, nonachlorobiphenyl 206; 10Cl, decachlorobiphenyl 209) was done by using individual standard congeners.

Appropriate blanks were analysed with each set of analyses and in addition, reference material IAEA-408 was analysed simultaneously. This sediment has certified concentrations of chlorinated compounds and hydrocarbons.

3. Results and discussion

With respect to interpretation of the results, a pragmatic approach was taken whereby the concentrations of organic contaminants in sediments were compared to North American sediment quality guidelines. Marine Sediment Quality Guideline values from NOAA's National Status and Trends Program (Long et al., 1995) designate an effects range low (ERL) and an effects range medium (ERM). The Canadian Interim Marine Sediment Quality Guidelines (ISQG) value and the Probable Effects Level (PEL) are defined by Environment Canada (ISQG, 1995). Several issues remain to be resolved with respect to sediment toxicity guidelines. The Caspian Sea is a unique system, being essentially a brackish lake with a salt composition that differs from that of seawater, for which sediment toxicity guidelines have yet to be established. Accordingly, the North American values were applied here with caution as a first step in assessing pollution in the Caspian Sea.

3.1. Chlorinated pesticides

Several chlorinated pesticides were analysed. The range of values is shown in Table 1 for four countries, together with the Canadian Interim Sediment Quality Guideline value for a number of these compounds. Generally the concentrations are not of concern, except for p,p'-DDT and its breakdown products, p,p'-DDE and p,p'-DDD. All three compounds exceed the ISQG values in Azerbaijan. However, elevated values were observed for only p,p'-DDE in Iran and p,p'-DDT in the Russian Federation. The concentration of lindane was also higher than ISQG for a few stations in the Russian Federation and must be of concern.

The concentrations of Σ DDTs (sum of DDT and the breakdown products DDD and DDE) are shown for all sites in Fig. 1. Noting that the NOAA effects range low (ERL) for DDTs is 1600 $\mathrm{pg\,g^{-1}}$, clearly DDT–type compounds exceeded this quality standard at a number of locations in Azerbaijan and Iran. The maximum value at station I-5 (13,400 $\mathrm{pg\,g^{-1}}$) showed a strong signal from the Kura River. The lowest concentrations were found in the North Caspian Sea, particularly in the northeastern shallow area. Recent results based on only 5 samples have also found low concentrations of p,p'-DDE (0.004–0.214 $\mu\mathrm{g\,kg^{-1}}$ wet) and p,p'-DDT (trace–1.00 $\mu\mathrm{g\,kg^{-1}}$ wet) in sediments from this region (Moore et al., 2003). Table 2 provides a basis for comparing the results reported here with other studies at several locations. Overall, the concentrations of Σ DDTs from the Caspian Sea sediments are quite comparable to levels found in Black Sea sediments from Turkey (0.2–7.2 $\mathrm{ng\,g^{-1}}$ dry) and the Russian Federation (3.3–12 $\mathrm{ng\,g^{-1}}$ dry, but much lower than the maximum levels (65 and 72 $\mathrm{ng\,g^{-1}}$ dry) measured in parts of coastal Ukraine and Romania that were directly influenced by discharges from the Danube River (Fillmann et al., 2002). Finally, it is noted that the elevated concentrations of Σ DDTs in sediments concur with recent evidence of widespread DDT contamination in Caspian seals (Vetter et al., 1995; Hall et al., 1999; Kajiwara et al., 2002; Watanabe et al., 1999).

Although previous studies in the Caspian Sea noted p,p'- DDT and its breakdown products as major contaminants in sturgeon (Södergren et al., 1978; Ballschmiter et al., 1983), national legislation has supposedly controlled the use of DDT in several riparian states for many years. The Caspian Sea was highlighted as one region in the Russian Federation receiving substantial Σ DDTs input during the period 1988–1996 (Zhulidov et al., 2000), but the riverine DDT concentrations in the Russian Federation did decline during the period from 1973 to 1996 (Zhulidov et al., 1998). While it would be comforting to ascribe the high content of Σ DDTs recorded here in sediments to historic usage, relatively high proportions of p,p'-DDT compared to p,p'-DDD and p,p'-DDE were evident at locations in each country (Fig. 2). This ternary diagram, showing the relative percentages of p,p'-DDT, p,p'-DDE and p,p'-DDD, illustrates that p,p'-DDT exceeds 50% of the Σ DDTs at several stations. Given the relatively slow degradation rate of DDT in the environment (Woodwell et al., 1971), such findings indicate recent DDT influxes and, by implication, ongoing DDT use throughout the region. The ratio of p,p'-DDT: p,p'-DDE provides a useful index to assess whether the DDTs at a given site is fresh or aged, a value <0.33 generally indicative of an aged input (Stranberg et al., 1998). As shown in Fig. 3, recently deposited DDT was evident through much of Kazakhstan, Russia, Azerbaijan and parts of Iran. Aged DDT was generally observed in the deeper sites and in the southeastern part of the Iranian coastal zone. In summary, DDT contamination of the Caspian Sea is highlighted as a contemporary and ubiquitous problem in the Caspian Sea.

The concentrations of total hexachlorocyclohexanes (Σ HCHs refers to the sum of all isomers measured) are shown for all sites in Fig. 4. The highest concentrations were observed in Azerbaijan, (196–3460 $\mathrm{pg\,g^{-1}}$) and the Russian Federation (99–807 $\mathrm{pg\,g^{-1}}$), as indicated in Table 1. Although widespread contamination of the Caspian Sea with respect to Σ HCHs has been concluded based on surveys of seals (Vetter et al., 1995; Kajiwara et al., 2002; Watanabe et al., 1999), data for Azerbaijan have generally been lacking. The mean concentration of Σ HCHs for the Caspian Sea sediments, 305 $\mathrm{pg\,g^{-1}}$, is not especially high by global standards (Table 2). The concentrations reported here are comparable to levels found through much of the Black Sea, outside the region in Romania downstream of the Danube River discharge (Fillmann et al., 2002).

Table 1
Chlorinated pesticide concentrations ($pg\,g^{-1}$)

Compound	Caspian Sea			Azerbaijan			Iran			Kazakhstan			Russian Federation			ISGS[a]
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	
HCB	66.1	<1	600	284	37	600	31.1	3	160	6.6	1.5	44	13	<1	73	
α-HCH	63	<0.6	1100	281	35	1100	24.1	1.5	160	2.6	<0.6	25	17	<1	48	
β-HCH	171	<1	1600	561	48	1600	123	24	390	16.9	2	230	123	<1	341	
Lindane	53.4	<0.6	609	74.7	10	240	7.5	1.5	39	2.4	<0.6	11	180	<1	609	320
δ-HCH	27.9	<0.9	520	110	21	520	5.1	2	33	1.2	<0.9	3.5				
Σ HCHs	305	4	3460	1028	196	3460	155	29	589	21.9	4	260	320	99	807	
p,p′-DDE	326	<0.5	1700	659	110	1300	542	9	1700	36.9	<0.5	1000	176	<1	639	1220
p,p′-DDD	287	<1	3400	866	210	3400	276	6	975	17.8	<1	410	205	<1	613	2070
p,p′-DDT	262	<1	7400	812	160	7400	196	13	615	9.1	2	190	258	<1	1796	4770
DDMU	135	<1	750	288	49	750	185	37	370	6.4	<1	170				
o,p′-DDE	24.9	<0.8	220	20	5	34	25.1	1.0	52	2.6	<0.8	8	63.3	<1	220	
o,p′-DDD	59.4	<1	440	118	3	440	84.5	2.5	240	7.3	2	100	53.2	<1	235	
o,p′-DDT	34	<1	410	34.8	7	77	39.7	4	270	5.8	2.5	35	70.8	<1	410	
Σ DDTs	1098	6	13,401	2798	560	13, 401	1335	57	3897	85.8	11.5	1896	827	6	1865	
cis Chlordane	7.2	<1	82	21.8	5	82	4.3	1.5	17	1.2	<1	4	<1	<1	<1	
trans Chlordane	18	<0.8	140	73	20	140	<2	<2	<2	0.9	<0.8	2	<1	<1	<1	
trans Nonachlor	30.7	<0.5	351	51.4	2	120	1.4	0.6	9	1	<0.5	12	101	<1	351	
Heptachlor	7.2	<0.5	88	3.6	2	10	1.8	0.6	6	0.5	<0.5	1	28.6	<1	88	
Heptachlor epoxide	22.3	<0.4	186	11.1	<1	45	10.8	<0.5	37	3.1	<0.4	16	78.6	<1	186	267
Σ chlordanes	80.3	3.2	504	161	40	310	20.3	6.6	62	6.6	3.2	22.1	208	33	504	
Aldrin	9.4	<0.4	77	21.2	2	77	14.2	0.6	65	3.7	<0.4	42	1.5	<1	11	
Dieldrin	14.4	<0.5	349	25.5	5	51	7	0.6	18	4.5	<0.5	32	30.3	<1	349	710
Endrin	16.6	<1	85	23.3	6	85	35.1	4	81	5.7	1.5	50	<1	<1	<1	267
Methoxychlor	97.5	<0.9	1476	83.9	3	330	44.8	1.5	150	5.1	<0.9	80	316	1	1476	
α-Endosulfan	4.7	<0.3	189	1.8	<1	16	3.4	<0.4	13	1.6	<0.3	14	13.3	1	189	
β-Endosulfan	3.9	<0.4	55	9.7	<1	22	2.9	<0.5	13	1.7	<0.4	7	3.6	1	55	
Endosulfan sulfate	7.6	<0.4	170	12.6	2	27	11.1	<0.6	170	1.9	<0.4	6				

[a] ISQG Canadian Interim Marine Sediment Quality Guidelines.

Table 2
World-wide concentration of Σ DDTs and Σ HCHs in sediments (ng g^{-1} dry wt)

Area	Survey year	Σ DDT (ng g^{-1})	Σ HCH (ng g^{-1})	References
Cities, Vietnam	1990	0.4–690	0.4–12	Iwata et al., 1994a
Rhone prodelta, Mediterranean Sea	1987–1988	62–675		Tolosa et al., 1995
Cities, India	1989	8–450	0.6–38	Iwata et al., 1994a
Coastline, United States	1986	0.01–454	0.01–0.77[a]	Wade et al., 1988
Xiamen Harbour, China	1993	4.5–311	0.1–1.1	Hong et al., 1995
South Western Coast, Baltic Sea	1993	<0.04–109	<0.04–5.0	Dannenberger and Lerz, 1996
Victoria Harbour, Hong Kong	1992	1.4-97	<0.1–9.4	Hong et al., 1995
Offshore Barcelona, Mediterranean Sea	1990	5–76		Tolosa et al., 1995
Romania Coastline, Black Sea	1995	0.6–72	0.2–40	Fillmann et al., 2002
Odessa, Black Sea, Ukraine	1995	35–65	1.3–2.3	Fillmann et al., 2002
Coastline, Adriatic Sea	1997	0.2–35		Picer, 2000
Cities, Japan	1990	2.5–12	4.5–6.2	Iwata et al., 1994a
Russian Federation coast, Black Sea	1995	3.3–12	0.3–0.8	Fillmann et al., 2002
North coast of Vietnam	1997	6.2–10.4	1.2–33.7	Nhan et al., 1999
Turkey coast, Black sea	1995	0.2–7.2	0.08–1.1	Fillmann et al., 2002
Deep basin of NW Mediterranean Sea	1990	1.4–5.5		Tolosa et al., 1995
Northern Baltic Sea	1991–1992	1.9–5.4	5.0–7.0	Strandberg et al., 1998
Gulf of Alaska, Bering Sea, Chukchi Sea	1990	0.01–0.2	0.04–0.3	Iwata et al., 1994b
Kara Sea	1993	Nd-1.2	Nd-0.6	Sericano et al., 2001
Northeastern Caspian Sea	1996	0.01–0.43 (wet)	0.01–0.25 (wet)	Moore et al., 2003
Caspian Sea, Azerbaijan	2000	0.56–13.4	0.20–3.5	This study
Caspian Sea, Russia	2000	0.01–1.9	0.01–0.8	This study
Caspian Sea, Iran	2001	0.06–3.9	0.03–0.6	This study
Caspian Sea, Kazakhstan	2001	0.01–1.9	0.01–0.3	This study

[a] lindane.

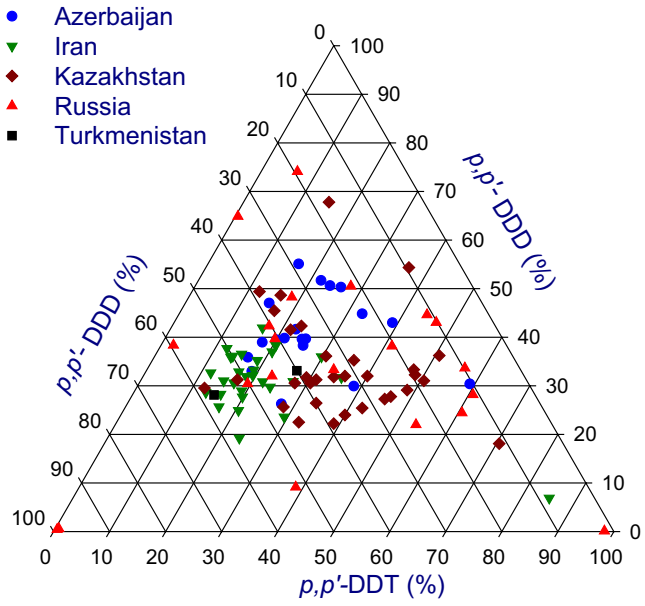

Fig. 2. Percentage of p,p'-DDT, p,p'-DDE and p,p'-DDD in Caspian Sea sediments categorised by country.

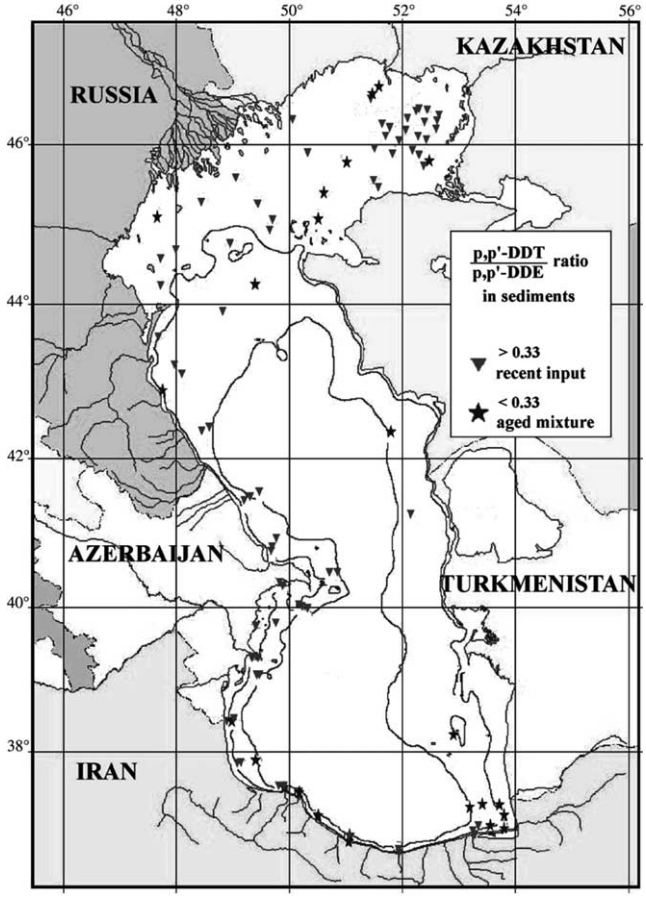

Fig. 3. The ratio of p,p'-DDT:p,p'-DDE in Caspian Sea sediments.

The maximum value, 3460 pg g^{-1}, is lower than the highest levels found along the Romanian coast (40 ng g^{-1}; Fillmann et al., 2002) in Vietnam (33.7 ng g^{-1}; Nhan et al., 1999) and in Hong Kong (9.4 ng g^{-1}; Hong et al., 1995). Iwata et al. (1994a) have reported elevated

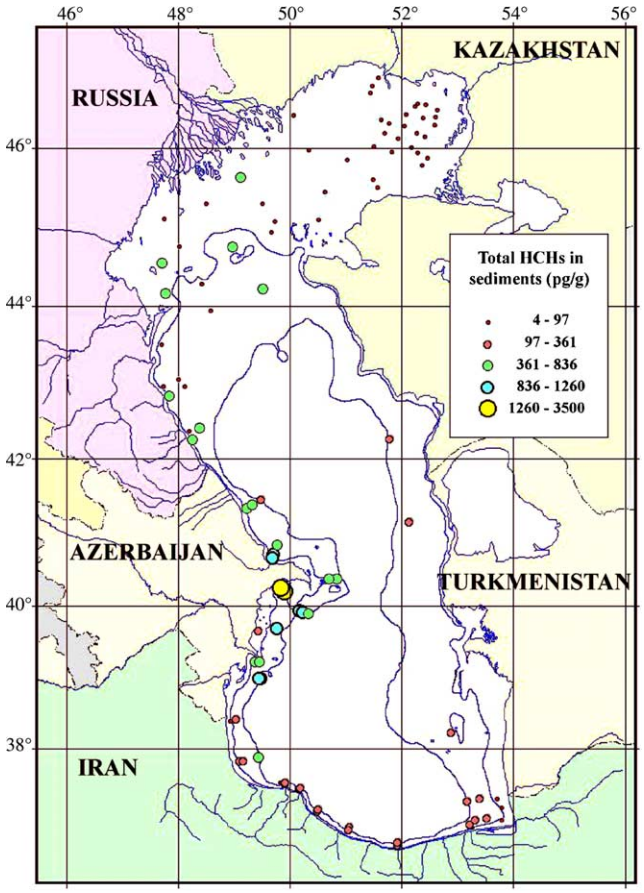

Fig. 4. Σ HCHs (pg g^{-1} dry wt) in coastal sediment from the Caspian Sea.

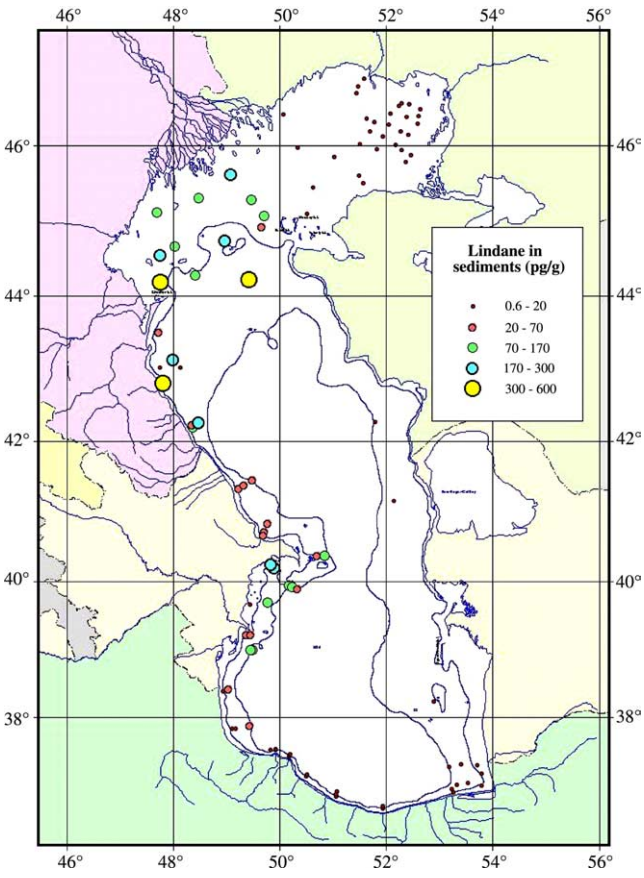

Fig. 5. Lindane concentrations (pg g^{-1} dry wt) in Caspian Sea sediments.

concentrations from cities in India (38 ng g^{-1}), Vietnam (12 ng g^{-1}), and Japan (6.2 ng g^{-1}).

There are eight steric isomers of HCH, of which three (α, β, and γ) are commonly mixed in varying amounts in pesticide formulations (Ballschmiter and Wittlinger, 1991). The isomer showing the highest insecticidal activity is lindane, which is γ-HCH. Fig. 5 illustrates the distribution of lindane concentrations in Caspian Sea sediments. Whereas the lowest values were found in the Iranian and Kazakhstan sectors, several stations in the Russian coastal zone had elevated levels. The maximum concentration 609 pg g^{-1}, exceeded the ISQG value of 320 pg g^{-1}. Lindane degrades relatively rapidly in the environment under both aerobic and anaerobic conditions (Rapport and Eisenreich, 1988, and references therein). Lindane also tends to be readily metabolised to water-soluble chlorophenols and chlorobenzenes upon ingestion by animals (Kennish, 1996). Therefore, high levels of lindane in the Caspian Sea sediments reflect the extensive and ongoing use of this compound in the Russian region. The widespread use of lindane in the Russian Federation has been documented (Zhulidov et al., 1998). Moreover, the Volga River and much smaller Terek River contribute comparable fluxes of γ-HCH to the Caspian Sea, the later owing to agricultural practices in the catchment region (Zhulidov et al., 2000).

Regarding the α- and β-isomers of HCH, the highest concentrations were found in Azerbaijan just south of Baku Bay (H-4-1 & H-5-1) for both compounds. Very low concentrations were measured in the northeastern sector, which is the shallow coastal zone of Kazakhstan. The relative amounts for the three main HCH isomers exhibit some regional differences in the Caspian Sea (Fig. 6). In particular, the dominance of lindane at several sites in the Russian Federation is evident. The relative amounts cannot be readily interpreted, being dependent upon the sources and relative degradation rates in the environment. Considering inputs, various HCH formulations have differing amounts of the α-, β-, and γ-isomers (Ballschmiter and Wittlinger, 1991) and long range atmospheric transport favours the more volatile isomer, α-HCH (Rapport and Eisenreich, 1988). However, β-HCH is the most resistant to microbial degradation and represents a good indicator of local, albeit aged, contamination (Willett et al., 1998). Except for one site in Azerbaijan (IS-3-2-1), the β-HCH concentrations exceed those of α-HCH in Caspian Sea sediments and are accordingly deduced to be local in

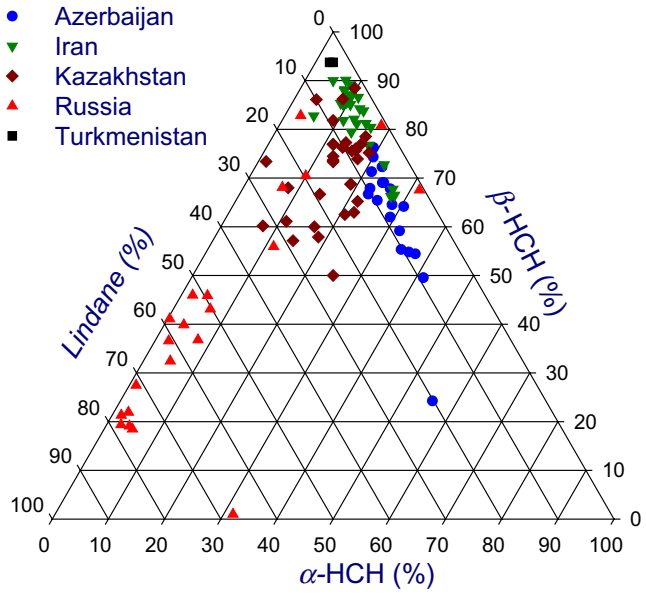

Fig. 6. Percentage of α-HCH, β-HCH, and γ-HCH (lindane) in Caspian Sea sediments classified by country.

origin. The high content of β-HCH in blubber of a seal (*Phoca caspica*) from coastal Iran was interpreted to be caused by local sources (Natzeck et al., 1995).

The concentrations of HCB in coastal sediments from the Caspian Sea are shown for all sites in Fig. 7. Whereas the highest concentrations, up to 600 pg g^{-1}, were observed in Azerbaijan, HCB was generally undetected (i.e. <1 pg g^{-1}) throughout the North Caspian Sea. There are no data from the Caspian Sea for comparison. Although HCB was detected in sturgeon muscle and eggs from the South Caspian Sea, no concentration levels were reported (Södergren et al., 1978). Similarly, another study of organochlorinated compounds in sturgeon from the Iranian sector of the Caspian Sea suggested that HCB was a major contaminant, but again no data were presented (Ballschmiter et al., 1983). A range of HCB studies at locations throughout the world are presented in Table 3. In this study, the HCB content in the Caspian Sea sediments is comparable to levels measured in Masan Bay, Korea (0.04–0.59 ng g^{-1}: Hong et al., 2003) and the Black Sea, other than the region influenced by the Danube River (Fillmann et al., 2002). Heavily contaminated sites have been shown to exhibit much higher HCB content in sediments, with maximum concentrations of 23 ng g^{-1} in Romania (Fillmann et al., 2002), 4.68 ng g^{-1} off Savannah, Georgia, USA (Loganathan et al., 2001), and up to 22 ng g^{-1} in sediment cores from the Mersey Estuary, UK (Fox et al., 2001).

Several other organochlorinated pesticides were measured in the sediment samples from the Caspian Sea, and the distribution ranges are presented in Table 1. Although the concentrations of other pesticides were not high as found for the DDTs and HCHs, and were generally not of concern (Table 1), three distinct distribution trends evidently reflected different usage patterns. Relatively elevated concentrations of *cis*- and *trans*-chlordane, aldrin and endrin were observed in the Azerbaijan sector. Within the Russian Federation methoxychlor, heptachlor, heptachlor epoxide, dieldrin, α-endosulfan, and β-endosulfan were notably higher in concentration than elsewhere in the Caspian Sea. Elevated amounts of endrin and endosulfan sulfate were generally observed in the Iranian sector. Moreover, national differences were observed, with endosulfan sulfate being high in the eastern region and aldrin relatively higher in the western part of the Iranian sector (data not shown).

3.2. Polychlorinated biphenyls (PCBs)

The total concentrations of PCBs (sum of 28 congeners) in 103 sediments from the Caspian Sea (Fig. 8) ranged from 0.03 to 6.4 ng g^{-1} with the highest amounts in the sectors of Russia and Azerbaijan. For comparison, various PCB studies are illustrated in Table 4. The PCB contents reported in this study are relatively low by global standards and do not exceed the NOAA Sediment Quality Guideline value for effects range low (ERL) of 23 ng g^{-1} dry wt (Long et al., 1995). The total PCB levels in Caspian sediments were lower than those found in the industrial/urban coastal environment of the United States (0.1 to 189 ng g^{-1}: Wade et al., 1988), Black Sea (0.06–72 ng g^{-1}: Fillmann et al., 2002), North Sea (3 to 20 ng g^{-1}: Klamer and Fomsgaard, 1993), Baltic Sea (1–214 ng g^{-1}: Dannenberger and Lerz, 1996; Konat and Kowalewska, 2001) and Mediterranean Sea (0.5–3200 ng g^{-1}: Tolosa et al., 1997; Picer, 2000). Concentrations of total PCBs <2 ng g^{-1} are common in marine environments where atmospheric deposition may prevail, such as the Gulf of Alaska (Iwata et al., 1994b), Kara Sea (Sericano et al., 2001), the coastline of Ukraine in the Black Sea (Fillmann et al., 2002) and in deep-basin sediments from the Northwestern Mediterranean Sea (Tolosa et al., 1995). The comparatively low concentrations of PCBs found in this survey also agree with the lower PCB concentrations reported in seals from the Caspian Sea compared to other worldwide regions (Hall et al., 1999; Watanabe et al., 1999; Kajiwara et al., 2002). From these comparisons it can be concluded that PCB pollution in the Caspian Sea is relatively low and without ecotoxicological concerns for the marine species inhabiting the Caspian Sea.

The highest concentration of PCBs (up 6.4 ng g^{-1} dry wt) was found in the vicinity of Makhachkala city on the Russia coast (station B-1), but the sediments immediately south of Baku Bay also contained relatively high concentrations (up to 3 ng g^{-1} dry wt). The PCB concentrations in these industrial and urban areas showed a negative gradient traversing from the inshore to offshore stations (e.g. transects from B-1 to B-2 and from H-5-1 to BP-3), reflecting localised sources of PCBs. In the

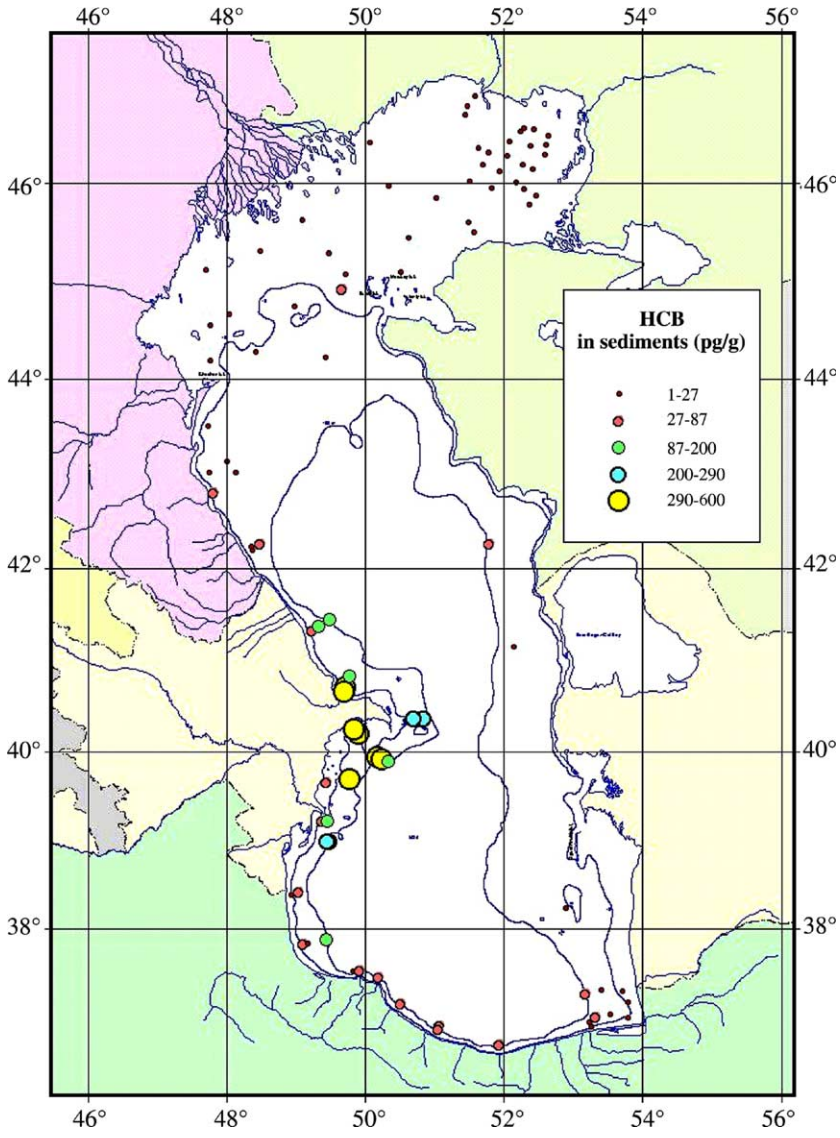

Fig. 7. The concentrations of HCB in coastal sediments from the Caspian Sea.

Table 3
Hexachlorobenzene (HCB) concentrations in sediments from different locations in the world

Area	Survey year	Concentrations (ng g^{-1} dry wt)	References
Rhone prodelta, Mediterranean Sea	1987–1988	11–39	Tolosa et al., 1995
Romania coastline, Black Sea	1995	5.3–23	Fillmann et al., 2002
Mersey estuary, UK		1–22	Fox et al., 2001
North Coast of Vietnam	1997	0.1–6.5	Nhan et al., 1999
Off Savannah, Georgia, USA	1997	<0.2-4.7	Loganathan et al., 2001
Offshore Barcelona, Mediterranean Sea	1990	0.4–2.9	Tolosa et al., 1995
South Western Coast, Baltic Sea	1993–1994	0.1–1.3	Dannenberger and Lerz, 1996
Coastline of Ukraine, Black Sea	1995	0.7-1.3	Fillmann et al., 2002
Northern Baltic Sea	1991–1992	0.8–0.9	Stranberg et al., 1998
Masan Bay, Korea	1997	0.04–0.6	Hong et al., 2003
Deep basin of NW Mediterranean Sea	1990	0.05–0.5	Tolosa et al., 1995
Coastline Russian Federation	1995	0.02–0.3	Fillmann et al., 2002
Gulf of Alaska, Bering Sea, Chuckchi Sea	1990	0.03–0.08	Iwata et al., 1994b
Caspian Sea, Azerbaijan	2000	0.04–0.6	This study
Caspian Sea, Iran	2001	0.01–0.2	This study
Caspian Sea, Russia	2000	0.01–0.07	This study
Caspian Sea, Kazakhstan	2001	0.01–0.04	This study

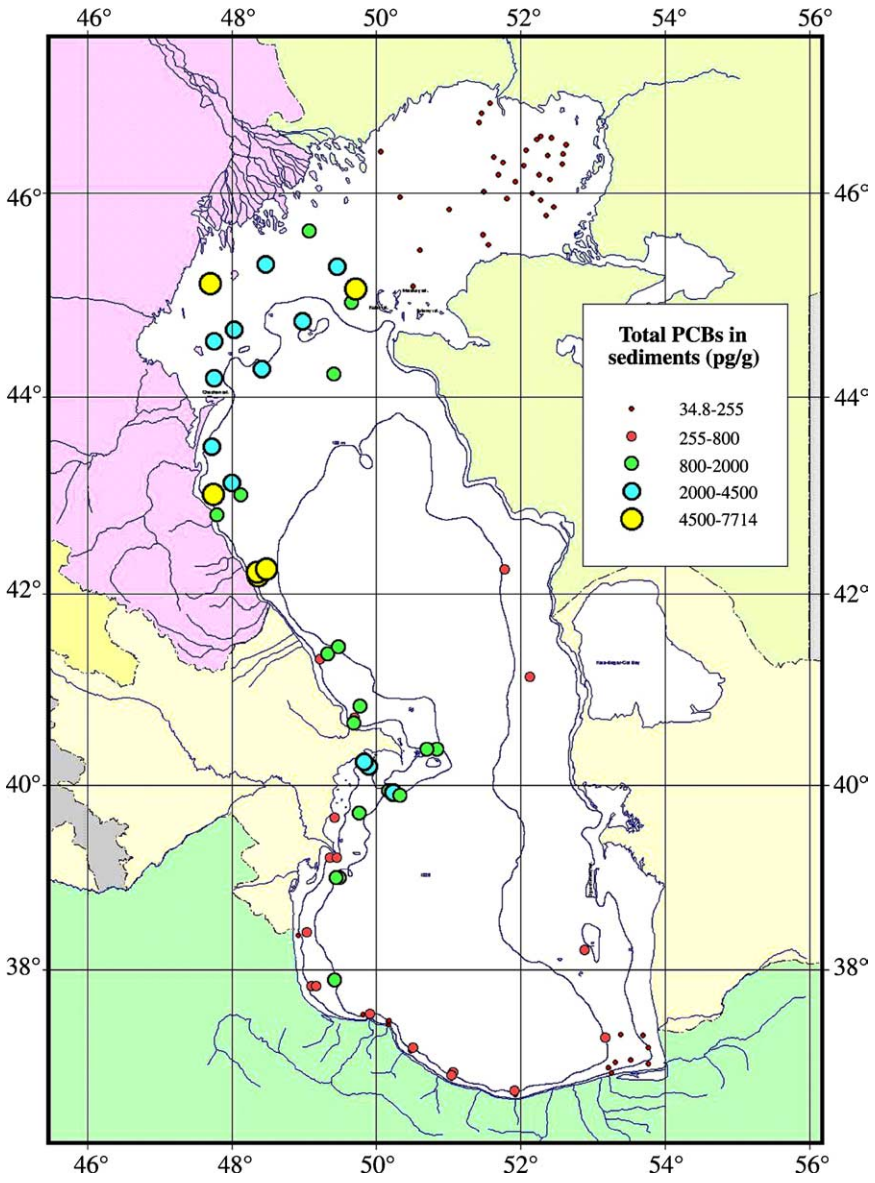

Fig. 8. Distribution of total PCBs (sum of 28 congeners) in sediments from the Caspian Sea (pg g^{-1} dry wt).

Iran and Kazakhstan sectors, the highest concentrations (up to 1 and 0.7 ng g^{-1}, respectively) were found at the deepest offshore sites (stations DP-1A and DP-6, respectively) that also contained the highest amount of TOC (1.9% and 2.8%, respectively). This feature may reflect long-distance transport of PCBs, since PCBs are known to have a strong sorption onto the fine particles (Duinker, 1986). The lowest levels of PCBs (<0.3 ng g^{-1}) were measured in the shallow and coarse sandy sediments of the Kazakhstan sector. This finding agrees with another recent study undertaken in the Kazakhstan area where levels of PCBs were below the detection limit of 5 pg g^{-1} dry sediment (Moore et al., 2003). Another limited study of Volga Delta sediments found that Σ PCBs (only 7 congeners) were below the detection limit of 0.04 μg g^{-1} (Winkels et al., 1998).

As already noted for PAHs (Tolosa et al., 2003), the Caspian sediment TOC contents did not correlate with the total PCBs suggesting that TOC in the Caspian Sea is affected by natural organic sources and/or other anthropogenic contamination. PCB concentrations normalized to the TOC (data not shown) showed a similar spatial variability for all regions with evidence of a higher PCB spot at the western part of Iranian coast (stations IS-5) and at the Russian sediments influenced by the Volga river discharges (stations A-8D, A-10, A-6).

The usage pattern and major sources of PCBs in the Caspian Sea are not well known, but Sovol and Trichlorodiphenyl (TCD) formulations, which are fairly close in composition to Aroclors 1254 and 1242, respectively, were used in the former Soviet Union and

Table 4
Polychlorinated biphenyls (PCBs) concentrations in sediments from different locations in the world

Area	Survey year	Concentrations (ng g^{-1} dry wt)	References
Coastline, Western Mediterranean Sea	1977–1990	0.5–3200 (Ar 1260)	Tolosa et al., 1997
Coastline, Adriatic Sea	1997	6–2203	Picer, 2000
Cities, India	1989	4.8–1000 (Kanechlors)	Iwata et al., 1994a
Cities, Vietnam	1990	0.2–630 (Kanechlors)	Iwata et al., 1994a
Cities, Australia	1990	0.5–790 (Kanechlors)	Iwata et al., 1994a
South Western Coast, Baltic Sea	1993–1994	1–214 (23 cong)	Dannenberger and Lerz, 1996
Southern Baltic Sea	1996–1999	1–149 (7 cong)	Konat and Kowalewska, 2001
Coastline, United States	1986	0.1–189	Wade et al., 1988
Victoria Harbour, Hong Kong	1992	3.2–81 (Supelco PCB mixture)	Hong et al., 1995
Masan Bay, Korea	1997	2.5–75 (18 cong×2)	Hong et al., 2003
Coastline, Black Sea	1995	0.06–72 (13 cong)	Fillmann et al., 2002
North coast of Vietnam	1997	0.5–28 (Ar 1254)	Nhan et al., 1999
Humber, Plume, North Sea	1990	3–20 (12 cong)	Klamer and Fomsgaard, 1993
Northern Baltic Sea	1991–1992	9–10 (68 cong)	Stranberg et al., 1998
Off Savannah, Georgia, USA	1997	2–9 (35 cong)	Loganathan et al., 2001
Xiamen Harbour, China	1993	0.05–7.2 (Supelco PCB mixture)	Hong et al., 1995
Volga delta	1993	<40 (7 cong)	Winkels et al., 1998
Deep basin of NW Mediterranean Sea	1990	1.1–2.5 (9 cong)	Tolosa et al., 1995
Gulf of Alaska, Bering Sea, Chuckchi Sea	1990	0.1–2 (36 cong)	Iwata et al., 1994b
Kara Sea	1993	n.d.-1.5	Sericano et al., 2001
Coastline of Ukraine, Black Sea	1995	n.d-0.4 (13 cong)	Fillmann et al., 2002
Northwestern Caspian Sea	1996	<2	Moore et al., 2003
Caspian Sea, Azerbaijan	2000	0.3–2.8 (28 cong)	This study
Caspian Sea, Iran	2001	0.1–0.8 (28 cong)	This study
Caspian Sea, Russia	2000	1.3–6.4 (28 cong)	This study
Caspian Sea, Kazakhstan	2001	0.03–0.6 (28 cong)	This study

would seem to be a logical source of PCBs in the Caspian Sea (Ivanov and Sandell, 1992). Sovol, the first Soviet technical PCB mixture, was first synthesized in the former USSR in 1934 and the estimated cumulative production and consumption of Sovol during the period from the 1940s to 1990s was about 100,000 ton (Ivanov and Sandell, 1992). The trichlorodiphenyl formulation was produced in the former Soviet Union during the 1960s–1980s, with an estimated total production of about 25,000 ton.

Typical chlorination level plots from the sediment samples and PCB commercial mixtures, such as those of Aroclor (Schulz et al., 1989) are illustrated in Fig. 9. Significant differences were observed in the distribution profiles of PCB congeners according to the chlorine substitution. Most profiles indicated that the PCBs in sediments were derived from more than one commercially available PCB mixture. Immediately south of Baku Bay (H-4-1 & H-5-1) and the two sediments from Turkmenistan (T-1 & T-3), the profiles were largely dominated by hexa-chloro, penta-chloro and hepta-chloro congeners reflecting a contribution of a highly chlorinated commercial formulation (e.g. Aroclor, 1260). A slight depletion of the highly chlorinated congeners was observed going offshore from south of Baku Bay due to the higher solubility and high vapour pressure of the lower chlorinated biphenyls, which are transported farther from the local point sources. In contrast to the region just south of Baku Bay, the distribution of PCB homologues in sediments from the Russian coastal zone most closely resembled the mixture Aroclor 1254 suggesting that Sovol was the origin. The congener profile in the rest of sites from Azerbaijan (Sumgait), Iran and Kazakhstan were very similar showing a dominance of Sovol with an admixture of the lower chlorinated species commonly derived from TCD, similar in composition to Aroclor 1242.

The observed distributional variability of PCBs clearly reflects source differences, which in most cases can be attributed to local point sources. However, atmospheric transport of the lower chlorinated species and the specific association of lower chlorinated congeners with the sand-size fractions and of highly chlorinated congeners with the finest fraction (Pierard et al., 1996) may also partly account for the different pattern observed between the regions.

The ratio of Σ PCBs to Σ DDTs provides a means to assess the relative importance of industrial and agricultural sources of chlorinated compounds in the environment. A small value indicates that the organochlorinated substances are predominantly derived from agricultural sources rather than industrial ones. The ratio for coastal sediments from throughout the Caspian Sea is shown in Fig. 10, together with the concentrations of Σ PCBs and Σ DDTs from which it is calculated. In Kazakhstan, the very low content of both Σ PCBs and Σ DDTs renders the index meaningless. Elsewhere, distinct differences are evident for the Russian sector compared to the coastal

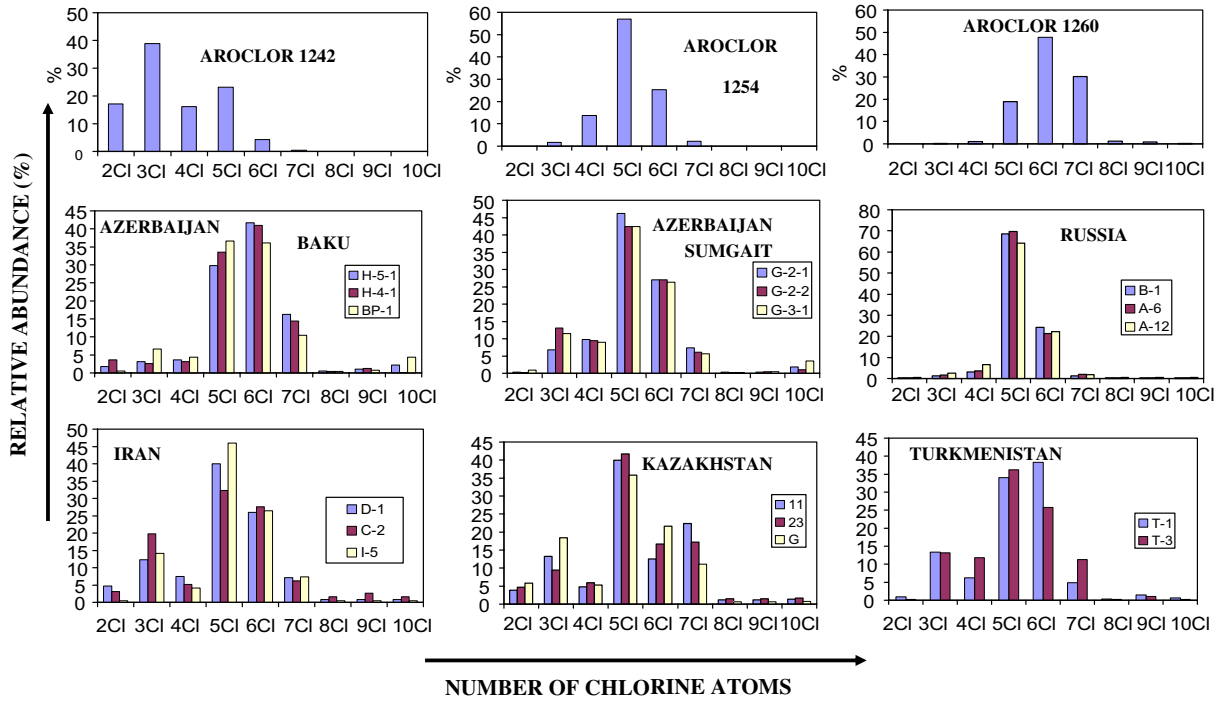

Fig. 9. Relative distribution of PCB congeners according to chlorine substitution (2Cl, dichlorophenyls 8; 3Cl, trichlorobiphenyls: 18, 28(+31), 4Cl, tetrachlorobiphenyls 44, 52; 5Cl, pentachlorobiphenyls 95(+66, 4Cl), 101, 105, 110(+77, 4Cl), 118, 126; 6Cl, hexachlorobiphenyls 128, 138, 149, 153, 156, 169; 7Cl, heptachlorobiphenyls 170, 180, 183, 187, 189; 8Cl, octachlorobiphenyl 195; 9Cl, nonachlorobiphenyl 206; 10Cl, decachlorobiphenyl 209) in the different areas of study. Aroclor commercial mixtures (Schulz et al., 1989) are also shown, but it should be noted that the composition of the two technical PCB mixtures commonly used in Russia, namely Sovol and TCD formulations, resemble Aroclors 1254 and 1242, respectively (Ivanov and Sandell, 1992).

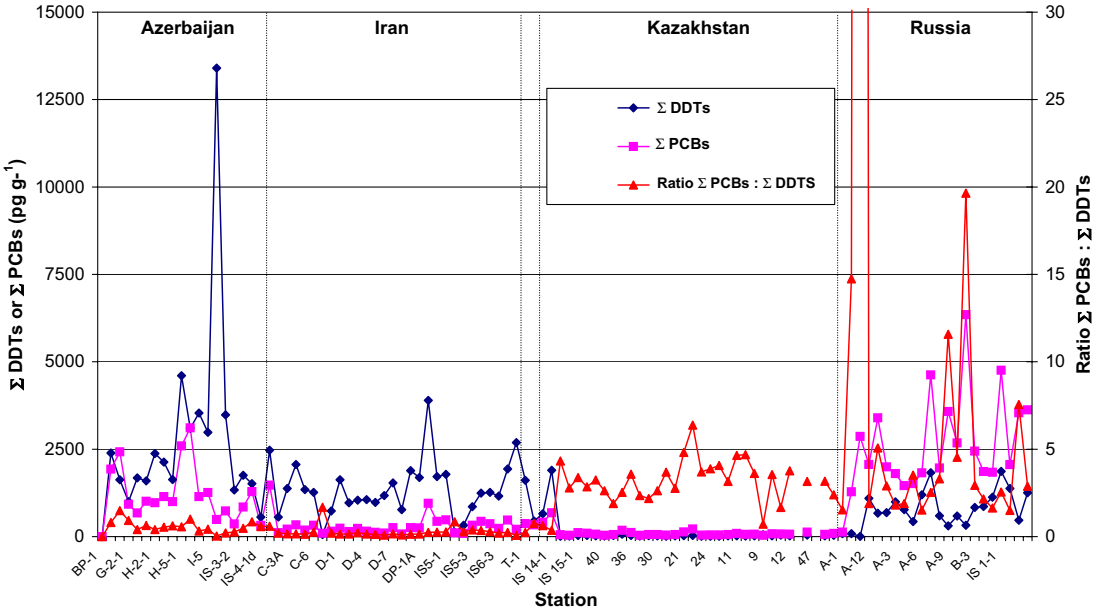

Fig. 10. The Σ PCBs to Σ DDTs ratio and concentrations of Σ PCBs and Σ DDTs for coastal sediments in the Caspian Sea.

regions of Azerbaijan and Iran. In the north, the high values reflect the relative importance of industrially derived PCBs. In contrast, the indices were quite low throughout Azerbaijan and Iran, highlighting the overall importance of agrochemical DDTs, especially in the vicinity of the Kura River.

4. Conclusions

A comprehensive survey of organochlorinated compounds, including several pesticides, in coastal sediments of the Caspian Sea was conducted. Sediment quality was interpreted on the basis of 103 samples collected in all littoral states, albeit only 2 samples were obtained in Turkmenistan. Generally the concentrations were not of concern, except for p,p'-DDT and its breakdown products, p,p'-DDE and p,p'-DDD. High concentrations for all three compounds were recorded in Azerbaijan. Elevated values were observed for only p,p'-DDE in Iran and p,p'-DDT in the Russian Federation. The percentage distribution of the three DDT-related compounds indicated that DDT contamination of the Caspian Sea constitutes a contemporary and ubiquitous problem in the Caspian Sea. Although the amounts of HCHs in Caspian Sea sediments, mean 305 $\mathrm{pg\,g^{-1}}$, were not especially noteworthy by global standards, high concentrations of lindane (up to 609 $\mathrm{pg\,g^{-1}}$) were found at some sites in the Russian Federation. The concentrations of HCB and other chlorinated pesticides (*cis*- and *trans*-chlordane, methoxychlor, heptachlor, heptachlor epoxide, aldrin, endrin, and endosulfans) were not high as found for the DDTs and HCHs, and were generally not of concern, but did demonstrate markedly different distributions reflecting differing agricultural usage in the region. The concentrations of Σ PCBs ranged from 0.03 to 6.4 $\mathrm{ng\,g^{-1}}$, with the highest amounts in the Russian and Azerbaijan. However, overall the PCB content in Caspian Sea sediments was relatively low by global standards.

Acknowledgements

The IAEA Marine Environment Laboratory operates under agreement between the International Atomic Energy Agency and the Government of the Principality of Monaco. Sediment samples from the coastal zone of the Caspian Sea were collected as part of the At Sea Training Programme from October 2000 to September 2001. We thank the crew of the *R/V Mammed Suleymanov*, *Gidrohimik*, *Issledovatel Kaspiya* and *Midiya* for the sample collection. This project was carried out under the auspices of the Caspian Environment Programme (CEP), with financial support from UNOPS and UNDP-GEF. Data from the Russian sector were provided by the "Typhoon" Center for Environmental Chemistry under contract to the CEP. We thank our colleagues, especially Tim Turner and Vladimir Vladymyrov, at the CEP Programme Co-ordinating Unit for their encouragement and support. Finally, with thank Jean Bartocci and Ziyafat Kerimov for assistance with producing the maps and figures.

References

Ballschmiter, K., Buchert, H., Scholz, C., Zell, M., 1983. Baseline studies of the global pollution: VI. The pattern of pollution by chlorinated hydrocarbons in the Caspian Sea. Fresenius' Zeitschrift für Analytische Chemie 316, 242–246.

Ballschmiter, K., Wittlinger, R., 1991. Interhemisphere exchange of hexachlorocyclohexanes, hexachlorobenzene, polychloro-biphenyls and 1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane in the lower troposphere. Environmental Science and Technology 25, 1103–111.

Dannenberger, D., Lerz, A., 1996. Polychlorinated biphenyls (PCB) and organochlorine pesticides in sediments of the Baltic and coastal waters of Mecklenburg-Vorpommern. German Journal of Hydrography 48, 5–26.

de Mora, S.J., Sheikholeslami, M.R., Wyse, E., Azemard, S., Cassi, R., 2004. An Assessment of Metal Contamination in Coastal Sediments of the Caspian Sea. Marine Pollution Bulletin 48, 61–77.

Duinker, J.C., 1986. The role of small, low density particles on the partition of selected PCB congeners between water and suspended matter (North Sea Area). Netherlands Journal of Sea Research 20, 229–238.

Dumont, H.J., 1995. Ecocide in the Caspian Sea. Nature 377, 673–674.

Dumont, H.J., 1998. The Caspian Lake: History, biota, structure, and function. Limnology and Oceanography 43, 44–52.

Fillmann, G., Readman, J.W., Tolosa, I., Bartocci, J., Villeneuve, J.-P., Cattini, C., Mee, L.D., 2002. Persistent organochlorine residues in sediments from the Black Sea. Marine Pollution Bulletin 44, 122–133.

Fox, W.M., Connor, L., Copplestone, D., Johnson, M.S., Leah, R.T., 2001. The organochlorine contamination history of the Mersey estuary, UK, revealed by analysis of sediment cores from salt marshes. Marine Environmental Research 51, 213–227.

Hall, A.J., Duck, C.D., Law, R.J., Allchin, C.R., Wilson, S., Eybator, T., 1999. Organochlorine contaminants in Caspian and harbour seal blubber. Environmental Pollution 106, 203–212.

Hong, H., Xu, L., Zhang, L., Chen, J.C., Wong, Y.S., Wan, T.S.M., 1995. Environmental fate and chemistry of organic pollutants in the sediment of Xiamen harbor and Victoria harbor. Marine Pollution Bulletin 31, 229–236.

Hong, S.H., Yim, U.H., Shim, W.J., Oh, J.R., Lee, I.S., 2003. Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. Marine Pollution Bulletin 46, 244–253.

Ivanov, V., Sandell, E., 1992. Characterization of polychlorinated biphenyl isomers in Sovol. Environmental Science and Technology 26, 2013–2017.

Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tatsukawa, R., 1994a. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. Environmental Pollution 85, 15–33.

Iwata, H., Tanabe, S., Aramoto, M., Sakai, N., Tatsukawa, R., 1994b. Persistent organochlorine residues in sediments from the Chukchi Sea, Bering Sea and Gulf of Alaska. Marine Pollution Bulletin 28, 746–753.

Kajiwara, N., Niimi, S., Watanabe, M., Ito, Y., Takahashi, S., Tanabe, S., Khuraskin, L.S., Miyazaki, N., 2002. Organochlorine and organotin compounds in Caspian seals (*Phoca caspica*) collected during an unusual mortality event in the Caspian Sea in 2000. Environmental Pollution 117, 391–402.

Karpinsky, M.G., 1992. Aspects of the Caspian Sea benthic ecosystem. Marine Pollution Bulletin 24, 384–389.

Kennish, M.J., 1996. Practical Handbook of Estuarine and Marine Pollution. CRC Press, New Jersey. pp. 524.

Klamer, H., Fomsgaard, L., 1993. Geographical distribution of chlorinated biphenyls (CBs) and polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Humber Plume, North Sea. Marine Pollution Bulletin 26, 201–206.

Konat, J., Kowalewska, G., 2001. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea-trends and fate. The Science of the Total Environment 280, 1–15.

Kosarev, A.N., Yablonskaya, E.A., 1994. The Caspian Sea. SPB Academic Publishing, The Hague. 259 pp.

Loganathan, B.G., Sajwan, K.S., Richardson, J.P., Chetty, C.S., Owen, D.A., 2001. Persistent Organochlorine Concentrations in Sediment and Fish from Atlantic Coastal and Brackish Waters off Savannah, Georgia, USA. Marine Pollution Bulletin 42, 246–250.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management 19, 81–97.

Moore, M.J., Mitrofanov, I.V., Valentini, S.S., Volkov, V.V., Kurbskiy, A.V., Zhimbey, E.N., Eglinton, L.B., Stegeman, J.J., 2003. Cytochrome P4501A expression, chemical contaminants and histopathology in roach, goby and sturgeon and chemical contaminants in sediments from the Caspian Sea, Lake Balkhash and the Ily River Delta, Kazakhstan. Marine Pollution Bulletin 46, 107–119.

Natzeck, C., Vetter, W., Luckas, B., Heidemann, G., Kiabi, B., Karami, M., 1995. Chlorinated hydrocarbons in the blubber of a seal (*Phoca caspica*) from the Caspian Sea. Chemosphere 30, 1685–1696.

Nhan, D.D., Am, N.M., Carvalho, F.P., Villeneuve, J.-P., Cattini, C., 1999. Organochlorine pesticides and PCBs along the coast of North Vietnam. The Science of the Total Environment 237/238, 363–371.

Picer, M., 2000. DDTs and PCBs in the Adriatic Sea. Croatia Chemica Acta 73, 123–186.

Pierard, C., Budzinski, H., Garrigues, P., 1996. Grain-size distribution of polychlorobiphenyls in coastal sediments. Environmental Science and Technology 30, 2776–2783.

Rapport, R.A., Eisenreich, S.J., 1988. Historical atmospheric inputs of high molecular weight chlorinated hydrocarbons to eastern North America. Environmental Science and Technology 22, 931–941.

Schulz, D.E., Petrick, G., Duinker, J.C., 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clorphen mixtures by multidimentional gas chromatography-electron capture detection. Environmental Science and Technology 23, 852–859.

Sericano, J.L., Brooks, J.M., Champ, M.A., Kennicutt II, M.C., Makeyev, V.V., 2001. Trace Contaminant Concentrations in the Kara Sea and its Adjacent Rivers, Russia. Marine Pollution Bulletin 42, 1017–1030.

Södergren, A., Djirsarai, R., Gharibzadeh, M., Moinpour, A., 1978. Organochlorine residues in aquatic environments in Iran, 1974. Pesticides Monitoring Journal 12, 81–86.

Stranberg, B., Van Bavel, B., Bergqvist, P.-A., Broman, D., Ishaq, R., Näf, C., Pettersen, H., Rappe, C., 1998. Occurrence, sedimentation, and spatial variations of organochlorine contaminants in settling particulate matter and sediments in the Northern part of the Baltic Sea. Environmental Science and Technology 32, 1754–1759.

Tolosa, I., Readman, J.W., Fowler, S.W., Villeneuve, J.P., Dachs, J., Bayona, J.M., Albaigés, J., 1997. PCBs in the Western Mediterranean. Temporal trends and mass balance assessment. Deep Sea Research II 44, 907–928.

Tolosa, I., de Mora, S.J., Sheikholeslami, M.R., Villeneuve, J.-P., Bartocci, J., Cattini, C., 2003. Aliphatic and Aromatic Hydrocarbons in Coastal Caspian Sea Sediments. Marine Pollution Bulletin, doi:10.1016/S0025-326X(03)00255-8.

Tolosa, I., Bayona, J.M., Albaigés, J., 1995. Spatial and temporal distribution, fluxes and budgets of organochlorinated compounds in NW Mediterranean sediments. Environmental Science and Technology 29, 2519–2527.

Vetter, W., Natzeck, C., Luckas, B., Heidemann, G., Kiabi, B., Karami, M., 1995. Chlorinated hydrocarbons in the blubber of a seal (*Phoca caspica*) from the Caspian Sea. Chemosphere 30, 1685–1696.

Wade, T.L., Atlas, E.L, Brooks, J.M., Kennicutt II, M.C., Fox, R.G., Sericano, J., Garcia-Romero, B., Defreitas, D., 1988. NOAA Gulf of Mexico status and trends program: Trace organic contaminant distribution in sediments and oysters. Estuaries 11, 171–179.

Watanabe, M., Tanabe, S., Tatsukawa, R., Amano, M., Miyazaki, N., Petrov, E.A., Khuraskin, S.L., 1999. Contamination Levels and Specific Accumulation of Persistent Organochlorines in Caspian Seal (*Phoca caspica*) from the Caspian Sea, Russia. Archives of Environmental Contamination and Toxicology 37, 396–407.

Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environmental Science and Technology 32, 2197–2207.

Winkels, H.J., Kroonenberg, S.B., Lychagin, M.Y., Marin, G., Rusakov, G.V., Kasimov, N.S., 1998. Geochronology of priority pollutants in sedimentation zones of the Volga and Danube delta in comparison with the Rhine delta. Applied Geochemistry 13, 581–591.

Woodwell, G.M., Craig, P.O., Horton, A.J., 1971. DDT in the Biosphere: Where does it go? Science 174, 101–1107.

Zhulidov, A.V., Headley, J.V., Pavlov, D.F., Robarts, R.D., Korotova, L.G., Fadeev, V.F., Zhulidova, O.V., Volovik, Y., Khlobystov, V., 1998. Distribution of organochlorine insecticides in rivers of the Russian Federation. Journal of Environmental Quality 27, 1356–1366.

Zhulidov, A.V., Headley, J.V., Pavlov, D.F., Robarts, R.D., Korotova, L.G., Vinnikov, Y.Y., Zhulidova, O.V., 2000. Riverine fluxes of the persistent organochlorine pesticides hexachlorocyclohexane and DDT in the Russian Federation. Chemosphere 41, 829–841.