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Pollutants in deep-sea organisms and sediments[1]

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Abstract

Analyses of pollutants, organochlorine residues and heavy metals (Cu, Zn, Mn, Cd, Pb, Hg) were carried out in deep-sea organisms, Asteridea, Holoturioidea, fishes. Heavy metals content was determined in sediments. Organochlorine residues were detected in all deep-sea organisms. However, the concentrations observed are similar to those for marine organisms from coastal areas. For heavy metals, high concentrations of mercury, up to 7.5 ppm/dry weight and 6.5 ppm are observed in echinoderms and sediment respectively. High concentrations of lead, up to 167 ppm, occur in the gills of fishes. For other metals, the values observed are roughly similar to those from the literature.

Pollutants in deep-sea organisms and sediments

Analyses of pollutants were carried out in deep-sea organisms, Asteridea, Holoturioidea and gadiform fishes, and deep-sea sediments from the northeast Atlantic ocean. Results show the presence of PCB and DDT residues in deep-sea organisms. Nevertheless, it appears that the concentrations of these residues are similar to those found in invertebrates of the same families sampled in unpolluted coastal areas and in gadiform fishes caught in the open sea. For heavy metals, high concentrations of mercury occur in the sediment and in the organisms. For other metals, Cu, Mn, Fe, Zn, Cd and Pb, the concentrations in the sediment are lower or similar to those observed for unpolluted coastal sediments.

At the present time, if it is possible to have a general view of the littoral pollution of most oceans and seas in the world, for water, sediments and marine organisms, only few results have been reported concerning the pollution of the deep part of the ocean. If for sediments some informations about metals are available (3), it must be noticed that for marine organisms, most of the works on this subject take into account only organisms sampled at depth less than 1500 m (4,5). For chlorinated hydrocarbons, essentially PCB's and DDT's, some informations have been reported for sea water and sediments from open ocean areas (6–11), whereas, only organisms, generally mesopelagic organisms, sampled at depth less than 1000 m have been considered.

The study of the deep part of the ocean presents a double interest. On one hand, it brings informations for the determination of reference levels, baseline studies, for heavy metals and chlorinated residues. On the other hand, it permits to determine the state of pollution of this part of the ocean which, on a volumetric point of view, is the most important of it.

Materials and methods

Marine organisms and sediments were sampled in four stations (Figure 1) during the "CNEXO-Intercalibration" cruise (August 1976) in the northeast Atlantic ocean, on the Porcupine abyssal plain, Biscay gulf and Rockal trench. All organisms analysed in this study were sampled with a trawl. The following species were analysed: *Dytaster agassizi*, *Styracaster horridus* and *Hyphalaster inermis* (asteridea); *Oneirophanta mutabilis*, *Pseudostichopus sp.* and *Psychropotes longicauda* (holoturioidea); *Antimora rostrata* (gadiform, gadidea) and *Coryphaenoides guentheri* (gadiform, macrouridea). The sediment was sampled with a "Reineck" core sampler.

Analyses of organochlorine residues. Biological samples were freeze-dried, grounded and extracted for 24 h with cyclohexane in a Soxhlet apparatus. The extract was then reduced by evaporation to about 3 ml. An aliquot, 0.5 ml, was removed and dried for determination of solvent extractable material weight. The remaining extract was cleaned by concentrated sulfuric acid. After shaking the two phases were separated by centrifugation at 3000 rpm. Quantitative analysis was carried out using an electron capture gas chromatograph (Tracor 560). The chromatographic column was packed with 10% DC 200 on chromosorb W, and operated isothermally at 200°C using nitrogen as carrier gas. Most samples contained PCB mixtures which closely correspond to phenochlor DP-5 and sometimes to phenochlor DP-6, so these commercial standards were used to quantify amount of PCB residues in biological samples. Seven major peaks, excluding pp' DDE peak, appearing on the gas chromatogram were used for quantification. Verification of the presence of DDT and DDD residues was confirmed by dehydrochlorination with alcoholic potassium hydroxyde on samples.

Analyses of heavy metals. For mercury, lyophylised biological samples were mineralised with nitric and sulfuric acid, followed by permanganate oxidation. After homogenization in a glass grounder, the sediment samples were mineralized with nitric acid followed by potassium permanganate oxidation. Total mercury in whole samples was analysed by flameless atomic absorption spectrophotometry using an UV monitor (Laboratory Data Control). For other metals, Cu, Mn, Fe, Zn, Cd, Pb, the lyophylised biological samples and the sediment were mineralized by successive adding of nitric acid, heated to dryness, recovered with 1 ml of hydrochloric acid, then appropriate dilution with bi-distilled water. Analyses were carried out with an atomic absorption spectrophotometre (IL 351), using an air-acetylene flamme, except for some Cd and Pb analyses which were performed by the flameless atomic absorption method in a graphite furnace. In all cases, for Hg and the other metals, the mineralization of

Table 1. Organochlorine residues contents in deep-sea organisms. Concentrations expressed as parts per billions (ppb)/fresh weight. ND = Not detected; [a] = PCB DP-5 profile; [b] = PCB DP-6 profile; ΣDDT = DDE + DDD + DDT.

Station	Species	% H_2O	Lipids/ dry weight	DDE	DDD	DDT	ΣDDT	PCB	PCB / ΣDDT
1	*Dytaster agassizi*	63.8	1.38	1.8	0.1	1.5	3.4	5.3[a]	1.5
1	*Hyphalaster inermis*	61.5	2.26	0.3	ND	ND	0.3	3.0[a]	6.2
1	*Styracaster horridus*	63.5	0.68	0.3	ND	0.1	0.4	2.8[a]	7.0
1	*Psychropotes longicauda*	95.2	1.07	0.8	ND	ND	0.8	0.5[a]	0.7
2	*Oneirophanta mutabilis*	77.5	0.09	0.2	ND	0.1	0.3	1.2[a]	4.0
3	*Oneirophanta mutabilis*	86.2	0.35	1.1	ND	1.2	2.3	3.2[a]	1.4
3	*Pseudostichopus sp.*	92.0	1.05	1.2	0.2	0.5	1.9	6.3[b]	3.3
4	*Antimora rostrata*								
	Muscle	80.5	0.51	2.0	ND	0.1	2.1	1.3[b]	0.6
	Liver	32.8	70.9	771.0	431.0	92.0	1294.0	1449.0[b]	1.1
	Gut	85.5	4.7	24.4	1.4	0.6	26.4	21.5[b]	0.8
4	*Coryphaenoides guentheri*								
	Muscle	80.7	0.91	2.0	0.1	0.1	2.2	1.8[b]	0.8
	Liver	55.	71.7	135.	47.	22.	204.	297.[b]	1.9

Table 2. Heavy metals content in deep-sea organisms. Concentrations expressed as parts per million (ppm)/dry weight. – in table = not analysed.

Station	Species	% H_2O	Cu	Mn	Fe	Zn	Cd	Pb	Hg
1	*Dytaster agassizi*	63.8	10.1	38.3	1028.	71.8	5.7	2.4	7.5
1	*Hyphalaster inermis*	61.5	25.0	185.	4025.	36.3	27.2	3.1	3.9
1	*Styracaster horridus*	63.5	53.2	268.	5098.	94.5	47.2	6.9	6.7
1	*Psychropotes longicauda*	95.2	14.7	50.5	1177.	27.9	4.9	7.9	4.6
2	*Oneirophanta mutabilis*	77.5	354.	305.	4918.	23.3	3.9	6.6	4.2
3	*Oneirophanta mutabilis*	86.2	134.	313.	4643.	20.1	4.9	2.3	0.47
3	*Pseudostichopus sp.*	92.0	27.2	287.	4431.	59.4	5.0	5.2	1.03
4	*Antimora rostrata*								
	Liver	32.8	20.5	1.5	101.	60.0	0.76	0.35	1.11
	Gall-bladder	88.0	25.0	5.4	67.9	67.9	0.25	0.75	–
	Gonads	–	9.2	8.3	121.6	431.	0.28	0.41	1.66
	Gut	85.5	19.6	14.1	1136.	190.9	6.7	2.89	1.34
	Muscles	80.5	3.5	3.5	19.2	15.3	0.06	0.30	2.23
	Gills	83.8	18.4	38.5	326.	113.	0.14	167.	0.53
	Kidneys	71.8	–	–	–	–	–	–	1.65
	Brain	41.4	–	–	–	–	–	–	0.36
4	*Coryphaenoides guentheri*								
	Liver	55.0	6.6	3.1	71.5	11.5	2.19	0.23	1.17
	Muscles	80.7	1.8	2.4	33.6	33.6	0.01	0.16	1.70
	Gills	80.5	37.0	75.0	204.1	140.1	0.24	40.3	2.18

the samples was carried out with ultra-pure chimical products. All sediments analysed were calcareous house. For each of them the fraction less than 63 μ was above 80%.

Results and discussion

The results of PCB and DDT residues analyses in the deep-sea biological samples are shown on table 1. The concentrations, expressed against wet weight, vary in asteridea from 0.4 to 3.4 ppb (parts per billions) for ΣDDT and from 2.8 to 5.3 ppb for PCB, DP-5. For holoturioidea these values are from 0.3 to 2.3 ppb for ΣDDT and from 0.5 to 6.3 ppb for PCB, DP-5, excepted one sample which presents a DP-6 profile. The residual levels in these two benthic families are roughly similar. pp' DDE residues are present in the seven samples analysed. On the other hand, pp' DDT is not detected in all samples and its levels are in all cases lower than those found for pp' DDE. pp' DDD residue is not detected, or only as a trace.

Few results have been reported in the literature about the concentration of chlorinated residues in these two types of invertebrate. Nevertheless, if we compare the results obtained by different authors (13–16) for asteridea and holoturioidea from various area, Irish sea, Nova Scotia, north Atlantic, gulf of Mexico, and from our study, bay of Biscay, it appears that the concentrations of PCB and DDT residues are roughly similar whatever the geographic area may be, coastal area or open oceanic area.

The two species of deep-sea fishes sampled on the west Scotland station (station 4) present very similar concentrations in muscle: 2.1–2.2 ppb for ΣDDT and 1.3–1.8 ppb for PCB. These concentrations are widely higher for liver: 204 and 1294 ppb for ΣDDT and 397 and 1449 ppb for PCB. It must be noticed that the liver of these two species presents a high lipids content, 70.9 and 71.7% respectively.

The results reported in the literature for gadiform fishes (11, 15, 17, 18) show that significant differences exist for organochlorine residues levels in the muscle of cods caught in coastal areas (ΣDDT: 10–30 ppb; PCB; 20–40 ppb) and in the muscle of those caught in the open sea, or in coastal areas with a low rate of pollution (ΣDDT: 3–6 ppb; PCB: 2–14 ppb). The concentrations of PCB and DDT residues in the muscle of the two deep-sea species are similar to those observed in cods from the open sea. On the contrary, it has not been noticed significant different concentrations of organochlorine residues in the liver of cods from coastal areas and from open oceanic water (18). The concentrations of DDT and PCB residues in the liver of the deep-sea fishes from station four are similar to those observed in the liver of cods.

The concentrations of heavy metals in biological samples are shown on table 2. It appears from this table that

high concentrations of mercury were found in all the organisms analysed, asteridea, holoturioidea, and also in the different organs of fishes. For lead, noteworthy concentrations occur in the gills of fishes. For other metals, results can be considered as similar to those found in the literature. Thus, if for Cd and Cu our values are slightly higher than for echinoderms from coastal areas, the concentrations are similar for Zn and lower for Pb (19–21). For fishes, Stenner and Nickless (19) analysed the gills and the muscle of many species from the Spanish and the Portuguese coast. In all cases the values reported for Cd are higher than our's. For Pb, Zn and Cu, the concentrations are similar. The concentrations of Zn and Cu, in the gills are similar too. Wright (22) analysed Cu, Zn and Cd in the liver, gills and muscle of fishes from the Northumberland coast. Among them are several species of gadiform fishes. It appears that the concentrations of Cu and Zn in these organs are similar to those in our study. For Cd, the values seem to be slightly lower for deep-sea fishes.

For mercury it is evident that the concentrations in deep-sea organisms are higher than those in organisms from unpolluted coastal areas. Thus, for the sole and the sardine, the mean concentrations of mercury are 0.042 and 0.026 ppm (parts per million)/wet weight respectively (23). Freeman and col. (24) showed that for Canadian Atlantic coast fishes the mercury content varied from 0.09 ppm for herring to 0.30 ppm/dry weight for sea raven respectively. For different species of pelagic fishes from northwest Africa and Azore areas, the mercury content varied from 0.04 to 0.25 ppm/dry weight (4). In our study the mercury content was much higher than that observed by these authors. Klein and Goldberg (25) analysed different organisms fromt he Californian coast. Most of them were epibenthic fauna. In that study the values range from 0.4 ppm/dry weight for a sea cucumber to 21 ppm/dry weight for a cowry sampled near a sewer outfalls. The mean value for the whole specimens in the study of Klein and Goldberg was 0.9 ppm/dry weight, while in our study this value was 4.1 ppm/dry weight for benthic animals, asteridea and holoturioidea. In the rade of Brest the mercury levels for the starfish *Marthasteria glacialis* and the sea cucumber *Palmipes membranaceus* are 0.78 and 0.12 ppm/dry weight respectively (Arima, unpublished data). These values are far from those observed for deep-sea echinoderms.

The marine organisms analysed in this study are benthic or bathy-pelagic organisms. It was interesting to determine the concentration of heavy metals in the sediment. For that purpose, only the upper two centimetres of the core were considered. The results are shown on table 3. If we compare these results to those from the literature concerning coastal sediments from England (26–31), Baltic sea (32), Australia (33), United States (25) or France (34), as well as deep-sea sediments from the Atlantic (35–37) or

Table 3. Heavy metals content in deep-sea sediments. Concentrations expressed as parts per millions (ppm)/dry weight.

Station	Cu	Mn	Fe	Zn	Cd	Pb	Hg
1	51.0	496	14 199	34.5	<0.04	7	6.0
2	48.2	552	10 700	23.9	<0.05	20.1	5.29
3	40.9	539	9591	22.1	<0.03	13.5	5.38
4	37.5	525	15 046	48.9	0.08	26.1	6.52

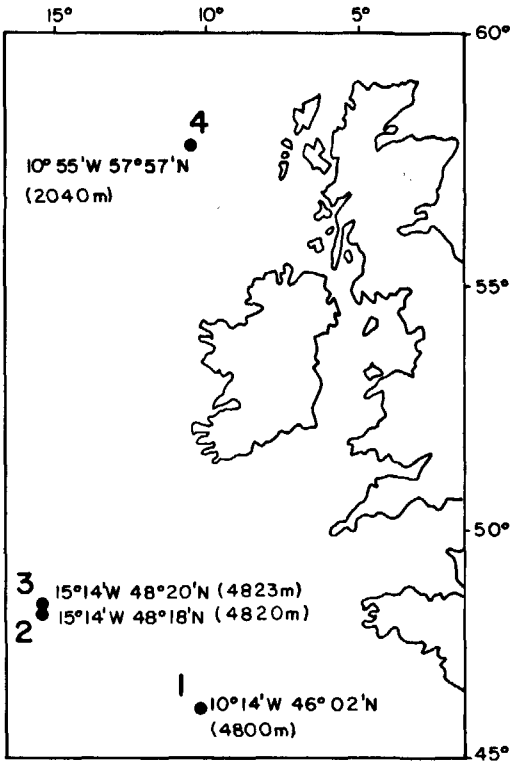

Fig. 1. Geographic location of sampling areas.

Pacific oceans (38, 39), it appears that except for mercury, all the values reported in this study are similar or lower than those from the literature.

The concentration of heavy metals in the sediment may provide explanations about the values observed for the organisms. Thus, for echinoderms, and more particulary for holoturioidea which ingest sediment, the high concentrations of Fe, Mn and Hg seem to be related to the concentration of these metals in the sediment. For fishes, the high mercury levels seem also to be related to the mercury content in the sediment. As a matter of facts, it has been shown that the deep-sea macrouridea live in contact with bottom or close to the bottom and they eat invertebrates and fishes caught in the epibenthic water layer and in the upper superficial sediment (40). The trophic transferts, from sediment to invertebrates, then from invertebrates to fishes may explain the high mercury content in fishes. It is also possible that these high mercury values be the consequense of the high mercury values in water. As a matter of fact, it has been shown (4) that the concentrations of mercury in open Atlantic ocean waters ranged from 0.017 μg/l to 0.142 μg/l, the highest concentrations occuring in deep water, more than 4000 m.

The concentrations of lead in the gills of the fishes are higher than those found in the sediment. Nevertheless, it is possible that a relation exists between the lead contents in the gills and in the sediment. It is known that metal ions set preferentially on the fine fraction of sediment. This study considered the total fraction of the sediment. It is then possible to suppose that the concentration of lead in the fine sediment fraction be widely higher than the one observed in the total fraction. The fine sediment which would be adsorbed on the gills of fishes would provide explanation for high lead values observed in this organ. As a matter of fact, Stenner and Nickless (19) showed that for a benthic fish such as the sole *Solea solea*, lead content in the gills reached 22 ppm/dry weight, while these authors

did not detected this metal in the gills of a pelagic fish such as the sardine *Sardina pilchardus*.

This study clearly demonstrates the presence of organochlorine residues in all deep-sea organisms analysed. Now, it is well known that the atmosphere is the mean way for transfer of chlorinated hydrocarbons to the ocean (41). Harvey and Steinhauer (7) have shown that PCB's are widely distributed in the surface and bottom water and in deep sediments of the Atlantic ocean. Similar observations were made for the Mediterranean sea (9). Informations about the west Scotland area, which correspond to station four in this study, tends to show that in this area the contamination is not negligible and is influenced by atmospheric precipitation, the north Atlantic current (6) and input, essentially by the Clyde estuary (42). On the other hand, few results have been reported concerning the Biscay bay, where most of the benthic invertebrates were taken from. Nevertheless, some results indicate the possibility of contamination of this area (18). However, it appears that the concentrations of PCB and DDT residues in the deep-sea organisms, asteridea and holoturioidea on one hand and gadiform fishes on the other hand are similar to those observed in invertebrates of the same kind from unpolluted coastal areas, and in gadiform fishes, cods more precisely, from open sea. It is not possible from our results to get informations about the residence time of organochlorine residues in the marine environment. Nevertheless, the presence of these compounds up to 5000 m depth lets suppose that their residence time must be very long to get time to reach such depths, through water movements, or more probably through trophic or particular transferts and to be assimilated by deep-sea organisms.

The presence of high mercury levels observed in deep-sea sediments analysed in this work seems to be more delicate to understand. Different hypotheses may be suggested in order to explain such concentrations. First, a contamination due to the use of a metallic core sampler. We can notice that high mercury levels are also observed in marine organisms, more precisely in invertebrates, which have been sampled with a trawl. Secondly, an error of analysis: it seems that such an hypothesis can also be dismissed. As a matter of fact, analyses of different sediments from the Bay of Brest, carried out in the same serie than the deep-sea sediments showed mercury values ranging from 0.015 to 0.16 ppm (Arima, unpublished data) which are considered to be normal values for unpolluted coastal sediments. The mercury observed in the deep-sea sediments analysed in this work can have different origins. If one suppose that this mercury is due to contamination from human activities, it is almost certain that these high levels would be accompanied by high values for other metals such as Cd, Pb, Zn and Cu for exemple, as it has been showed for coastal areas. It would seem as a matter of fact, that the high mercury values may be from a natural origin. It has been showed (39) that mercury could have a natural origin, for exemple in areas of active sea floor spreading. Nevertheless, it must be noticed that the sediments and organisms analysed in this work were sampled far from any recent spreading zone. Further studies are necessary to confirm the high mercury values observed in this work, and particulary, it seems necessary to analyse the mercury content in depth of cores sampled in these areas, to determine the evolution of mercury content with time. Such a study would provide informations ont he origine of the mercury in deep-sea sediments.

References and notes

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