Heavy Metals in Water, Sediments and Biota in Dumping Areas for Acid Wastes from the Titanium Dioxide Industry

by

M. BAETEMAN
W. VYNCKE
Ministry of Agriculture, Fisheries Research Station
Ankerstraat, 1, B-8400 Oostende

R. GABRIELS
Ministry of Agriculture, Governmental Station for Ornamental Plants
Caritasstraat, 17, B-9230 Melle

M. GUNS
Ministry of Agriculture, Institute for Chemical Research
Museumlaan, 5, B-1980 Tervuren

Belgium

International Courcil for the Exploration of the Sea, Copenhagen.
Marine Environmental Quality Committee C.M. 1987/E:7.

International Council for the
Exploration of the Sea

C.M. 1987/E : 7
Marine Environmental Quality Committee

Heavy metals in water, sediments and biota in dumping areas for acid wastes from the titanium dioxide industry

M. Baeteman
W. Vyncke

Ministry of Agriculture, Fisheries Research Station
Ankerstraat, 1, B-8400 Oostende

R. Gabriels

Ministry of Agriculture, Governmental Station
for Ornamental Plants
Caritasstraat, 17, B-9230 Melle

M. Guns

Ministry of Agriculture, Institute for Chemical Research
Museumlaan, 5, B-1980 Tervuren

Belgium

ABSTRACT

The results of a four years' period (1981-1984) of monitoring heavy metals in two dumping sites for titanium dioxide waste off the Belgian coast are reported. For comparison, two reference areas were also monitored. Neither in the water, nor in the sediments nor in biota (epibenthos and fish) an increase in heavy metal content could be noted.

RESUME

Les résultats d'une période de quatre ans (1981-1984) de surveillance des métaux lourds dans deux sites de déversement de déchets de l'industrie du dioxyde de titane sont donnés. A titre de comparaison deux zones de références furent également inclus dans l'étude. Ni dans l'eau, ni dans les sédiments ni dans la biote (epibenthos et poisson) une augmentation du taux de métaux lourds put être détectée.

1. INTRODUCTION

The discharge of wastes from the titanium dioxide industry is a potential threat to the marine environment owing to the large quantities of acid and heavy metals involved. International regulatory organizations have given priority to this problem (Oslo Commission 1985a, b ; EEC 1978, 1982).

Two factories are dumping titanium dioxide waste off the Belgian coast. The first plant carried out disposal operations from 1961 till 1982 in area D1a (fig. 1). In 1983 the site was moved slightly to the South-West (D1b) due to a change in traffic separation lanes. The second factory started dumping in 1970 in area D2. In both areas dumpings were carried out almost daily. This lasted until 1985, when a new area in the Northern part of the Belgian Continental Shelf was designated for both factories by the Ministry of the Environment.

An average of 600.000 t per year was discharged (about 50 % for each factory), consisting of 120.000 t sulphuric acid, 12.000 t iron, 1.800 t aluminium, 1.200 t titanium, 300 t vanadium, 100 t chromium, 3 t zinc and 50-500 kg of copper, lead, nickel and other trace elements.

The dumping areas are characterized by strong tidal currents, prevailing NW-winds and frequent storms. There is a residual NE-current with a speed of 5 cm/sec and a flow of 15-25 m^3/sec (Mommaerts and D'Hondt 1986). This favourable hydrodynamic pattern guaranteed a thorough mixing. A dilution of 1 : 1.000 after 10 sec and 1 : 80.000 after 20 min was noted (Roekens and Van Grieken 1983), which was markedly higher than e.g. in the German Bight (Weichart 1977).

Due to the alcaline pH of seawater however, iron precipitates as iron (III) hydroxide and other metals may coprecipitate. Hence, an increase of heavy metals with varying toxicity in sediments and biota cannot be excluded.

Calculations by ICES (1984) have demonstrated that while deleterious sub-lethal effects on marine organisms and compositional changes in sediments caused by the disposal of wastes from the titanium dioxide industry are unlikely to occur throughout the North Sea as a whole, effects on smaller areas within the coastal zones of countries carrying out these waste disposal practices could be expected.

The investigations were started in 1976 and an internal report for the period 1976-80 was published indicating no detrimental effects to the invironment (Baeteman et al. 1982).

This paper reports the results of investigations carried out during 1981-84 on water, sediments and biota in and around the two dumping sites and in two reference areas (fig. 1 : R1 and R2). The determinations were performed taking into account the guidelines of the Oslo Commission (1985 a, b) and the directives of the EEC (1978, 1982).

As several analytical methods were changed (e.g. extraction techniques for sediments), results are not always directly comparable with the data for 1976-1980.

In the same period a biological monitoring was also carried out in the four areas. The results of the latter will be published separately.

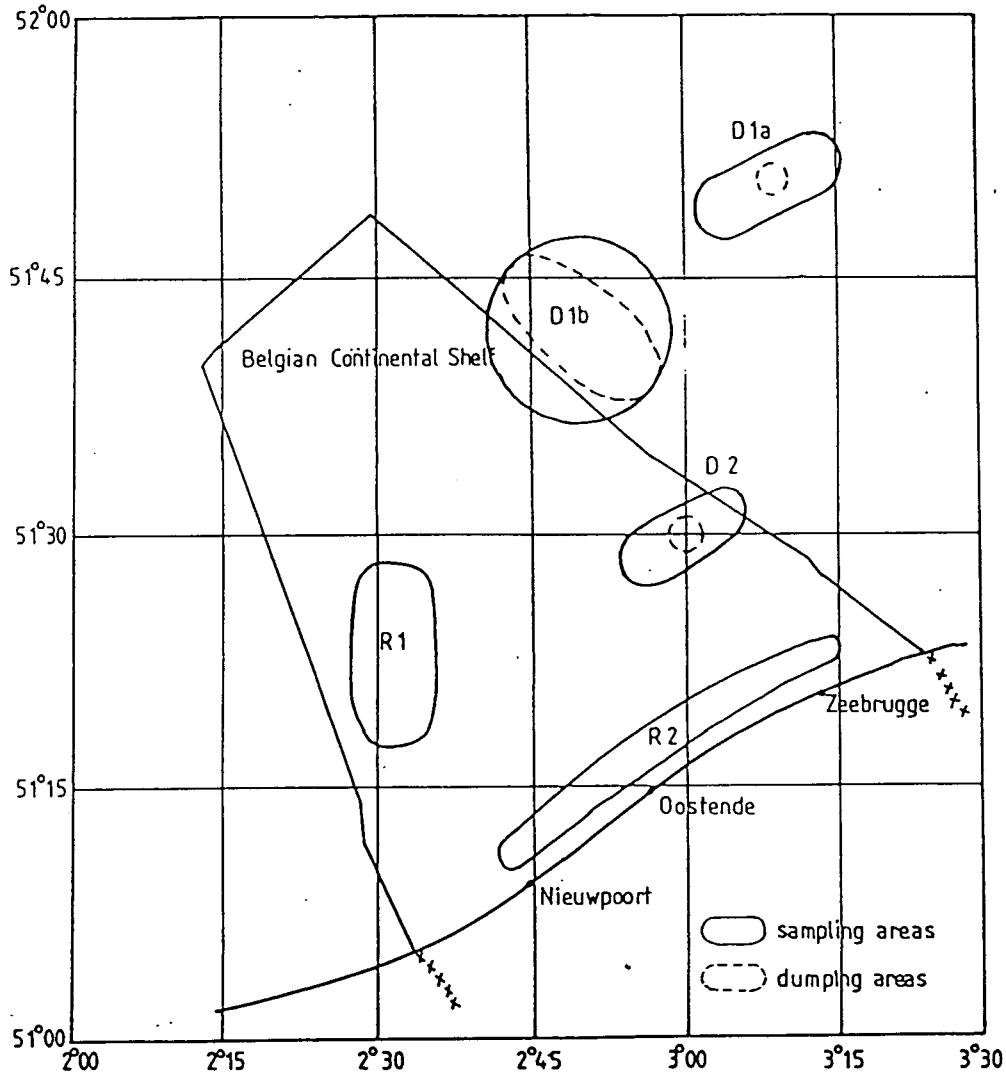

Figure 1 - Dumping and sampling areas (D : dumping areas, R : reference areas)

2. MATERIALS AND METHODS

2.1. Water.

Three samples were taken with a Niskin sampler at about 1 m from the bottom in each area three times a year. Dissolved oxygen was determined by the Winkler method (APHA 1976). Total iron was assessed with the ferrozine method (Stoockey 1970).

Other metals were not determined, but according to Weichart (1975), iron can be taken as a tracer characterizing the behaviour of titanium, manganese, chromium, aluminium and possibly that of vanadium.

2.2. Sediments.

Ten samples were taken with a Van Veen-grab in each area once a year. They were kept at -28 °C until analysis. As most metals are associated with the mud fraction and according to the recommendations of ICES (1983), the $< 63\ \mu m$ fraction was separated in a first sub-sample by wet sieving. The percentages of this fraction in the sediment are reported in table 1 together with the organic matter content, carbonate content and salinity of the water (Vandamme and Gabriels 1983). In a second sub-sample, particles larger than $500\ \mu m$ were removed (maximum 5 %). The latter could thus be regarded as representing the total sediment.

- Extraction procedures.

Two procedures were chosen : (1) extraction of the total metal content by digestion with hydrofluoric acid and (2) extraction of the exchangeable metal fractions with acetic acid 25 %.

For the extraction of the total metal content a 100 mg sample was digested for two hrs at 100 °C in a teflon bomb with 6 ml hydrofluoric acid, 0,15 ml nitric acid and 0,75 ml hydrochloric acid.

Acetic acid extractions was performed by shaking 2 g of sediment for 24 hrs at room temperature with 25 ml acetic acid (25 %). The suspension was centrifuged and the residue was washed with 10 ml bi-distilled water.

- Determination of heavy metals.

The main metals present in the waste were determined : Fe, V, Cr and Zn by atomic absorption spectrometry (Gabriels 1973), Al by spectrofluorimetry (Gabriels et al. 1981) and Ti by UV-VIS spectrophotometry (Gabriels et al. 1983).

2.3. Biota.

Sea star (Asterias rubens), hermit crab (Pagurus bernhardus), swimming crab (Macropipus holsatus) and brittle star (Ophiura texturata) were collected once a year. Bulked samples of 6 to 10 animals were taken for analysis.

In 1982 10 specimens of plaice (Pleuronectes platessa), flounder (Platichthys flesus), whiting (Odontogadus merlangus), cod (Gadus morhua) and 50 specimens of shrimp (Crangon crangon) were also investigated. All samples were kept at -28 °C prior to analysis.

Benthic organisms were finely chopped and analysed whole. Only the muscle tissue of the fish samples was taken.

Table 1 - Percentages (average and range) of the $< 63\ \mu m$ fraction, organic matter content, calcium carbonate content in the sediments and salinity of the water

Area	$< 63\ \mu m$ (%)	Organic matter (%)	Calcium Carbonate (%)	Salinity (‰)
D1a	0,6 (0,1-1,1)	0,26 (0,16-0,34)	3,7 (2,6-5,3)	33,6 (32,3-34,2)
D1b	1,0 (0,8-1,2)	0,34 (0,15-0,55)	7,8 (3,9-14,2)	34,0 (32,3-34,8)
D2	9,8 (1,1-32,5)	1,43 (0,48-3,90)	13,5 (8,2-24,9)	32,9 (30,9-34,5)
R1	2,0 (1,0-6,6)	1,28 (0,27-2,40)	17,7 (11,6-23,8)	32,8 (29,5-34,1)
R2	28,7 (1,3-86,6)	2,54 (0,47-6,15)	18,5 (7,5-34,9)	33,8 (32,6-34,6)

Fe, Ti, Cr, Zn, Ni, Pb, the analysis of which is mandatory by the EEC (1982) were determined as well as Hg, Cd and Cu which are currently assessed on a routine basis in marine organisms off the Belgian coast (optional for EEC).

Analyses of the heavy metals were carried out with atomic absorption spectrometry after digestion of the ashed samples with concentrated nitric acid.

Mercury was determined by cold vapour atomic absorption spectrometry after digestion of the fresh samples with sulphuric acid (Vanderstappen et al. 1978).

Titanium was extracted from the fresh samples with concentrated sulphuric acid and ammoniumsulphate, and determined after precipitation as Ti $(OH)_4$ with X-ray fluorescence spectrometry.

3. RESULTS AND DISCUSSION

3.1. Water.

Overall results are illustrated in fig. 2.

A lack of dissolved oxygen was never observed and no marked differences between the four areas were noted indicating that the oxidation of Fe^{++} had no measurable consequences in the water column. This appears not to be the case in other titanium dioxide waste dumping areas. Oxygen deficiencies were locally detected in the near-bottom water of the German Bight, especially in summer, due to lesser mixing of the water column. It is not to be excluded that discharges of titanium dioxide wastes are partially responsible (Dethlefsen and von Westernhagen 1983).

The iron content was very similar in both the dumping areas and in reference zone 1 (ca 0,05 mg/l). In the coastal area (D2) however, the concentrations were 2 to 5 times higher, showing the influence of river inputs. This was also observed by Roekens and Van Grieken (1983). Dutch investigators found similar mean values in a titanium dioxide waste dumping site and concluded that it was not possible to detect an increase in iron concentration due to the waste discharge (Spaans 1985). In the German Bight, higher concentrations of up to 1 mg/l were found near the disposal area, due to a less favourable hydrodynamic pattern (Weichart 1975, Schmidt 1980).

Abnormally low pH-values were not noted. It has been shown repeatedly that a short time after discharge, pH-values became normal again (Weichart 1977, Roekens and Van Grieken 1983 ; Knutzen 1983 ; Ambio 1987).

In the two dumping sites and in reference zone 1 mean pH-values were between 8,1 and 8,3. In the coastal area (R2) however the values were 0,1 - 0,2 units lower again indicating the influence of land-based pollution sources.

Compared to the 1976-80 data (Baeteman et al. 1982) for the dumping areas there were no significant differences in iron-, pH- and oxygen values.

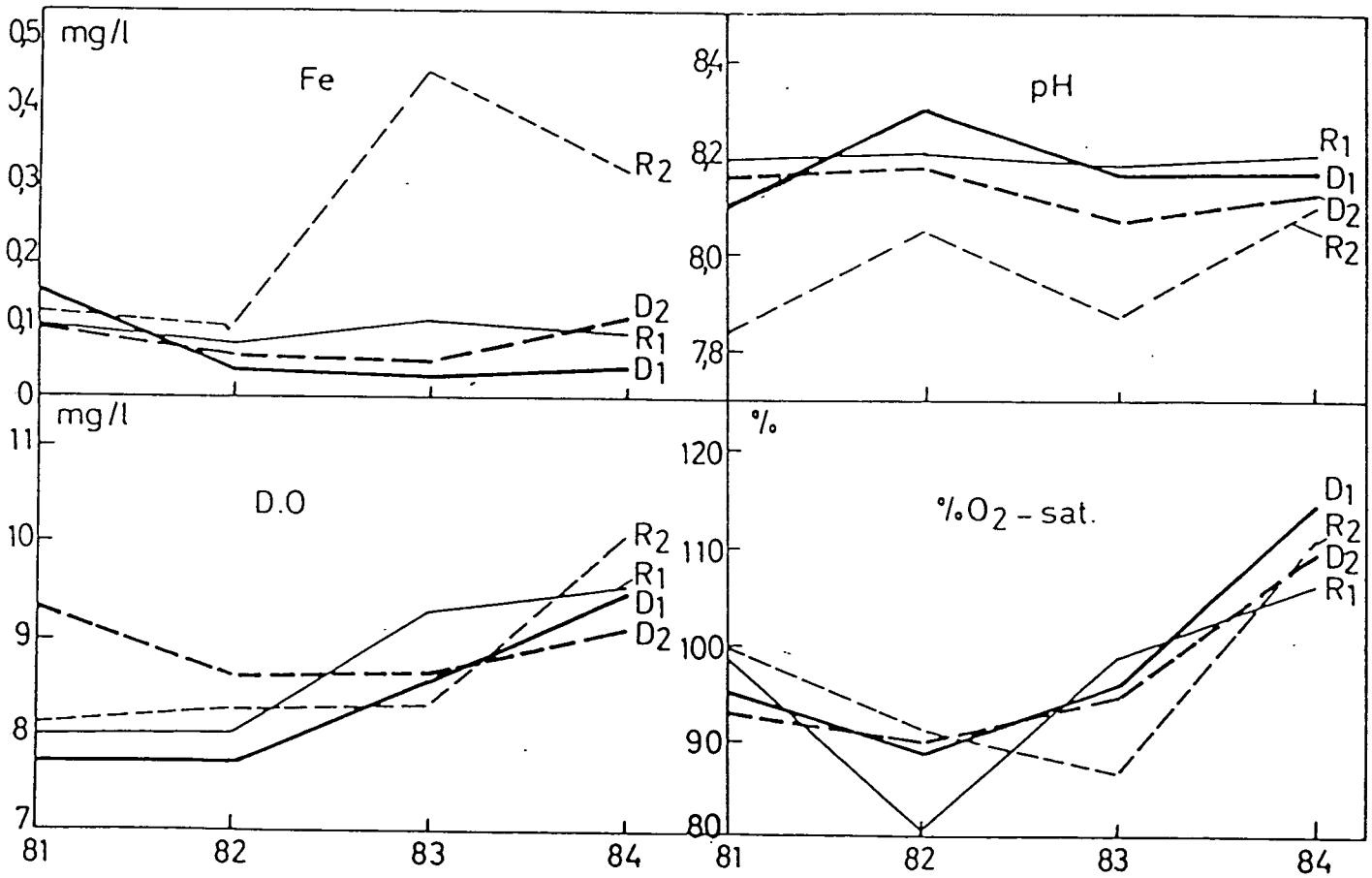

Figure 2 - Evolution of iron content, pH, dissolved oxygen (D.O.) and % oxygen saturation in the water

3.2. Sediments.

3.2.1. Total destruction.

Fig. 3 shows the evolution of the concentrations of heavy metals over the four years' period. The average contents together with the relative standard deviations are reported in table 2.

For both fractions and despite large fluctuations of the relative standard deviations (mostly between 20 and 50 %) it can be concluded that with the exception of zinc, the lowest heavy metal contents were found in dumping area D1, the latter being farthest from the coast. This was confirmed by analysis of variance on the average values (95 % probability level). In area D2, values fluctuated around those of reference areas R1 and R2. No clear temporal trend could be detected.

As already mentioned for the water column, the concentrations of heavy metals did not appear to be linked directly to the disposal of titanium dioxide waste but to input sources in general. The distance to the coast seems to play an important role. The mud fraction which varied greatly (table 1) also had an influence on their concentration. In this respect it should be noted that the coastal area R2 had the highest total load when considering the $< 500\ \mu m$ fraction (confirmed by analysis of variance), but not when the $< 63\ \mu m$ fraction was taken into account separately. In this case, the values were generally lower than those found in areas D2 and R1. Interference due to the higher organic matter content (table 1) was also possible, caused by the scavenging effect towards heavy metals (ICES 1983).

The question arises if the $< 63\ \mu m$ fraction is the best basis for estimating the contamination load by heavy metals. In the case of the Belgian coastal waters, the "total fraction" could be more appropriate. Especially when contaminants are associated with a coarser fraction, which seems to be the case here, it is recommended to analyze the latter (ICES 1983).

Another argument in favour of choosing the $< 500\ \mu m$ fraction is to avoid the difficulty of complete separation of the mud fraction. Large proportions of finer grain-size fractions can adhere to coarser particles thus giving a wrong picture of the distribution of heavy metals (Wall et al. 1978).

Comparison with other published results is rather difficult due to differences in analytical techniques, extraction methods, fractions selected, etc. However, determination of Cr, Ti, V and Fe in the $< 16\ \mu m$ fraction of a Dutch titanium dioxide waste dumping ground gave quite similar results (Spaans 1985). Levels of Fe, Ti and Mn, as elements characteristic of the titanium dioxide wastes, in the discharge area in the Gulf of Cadiz, were not significantly different from those found in areas of the continental slope far from the disposal area (Ambio 1987). No enrichment of iron or other metals was observed in the sandy sediments of the New York Bight dumping area (Vaccaro et al. 1972). In the German Bight however Fe-, Cr and V-values of respectively 80.000, 100 and 370 mg/kg were observed in the $< 20\ \mu m$ fraction. This proved to be 1,5 to 4 times higher than in adjacent areas (Deutsches Hydrographisches Institut 1984).

It should be remarked that discharging through fixed pipelines increases the concentration of heavy metals in both the surface sediments and the water in the vicinity of several European titanium dioxide waste outfalls (Knutzen 1983).

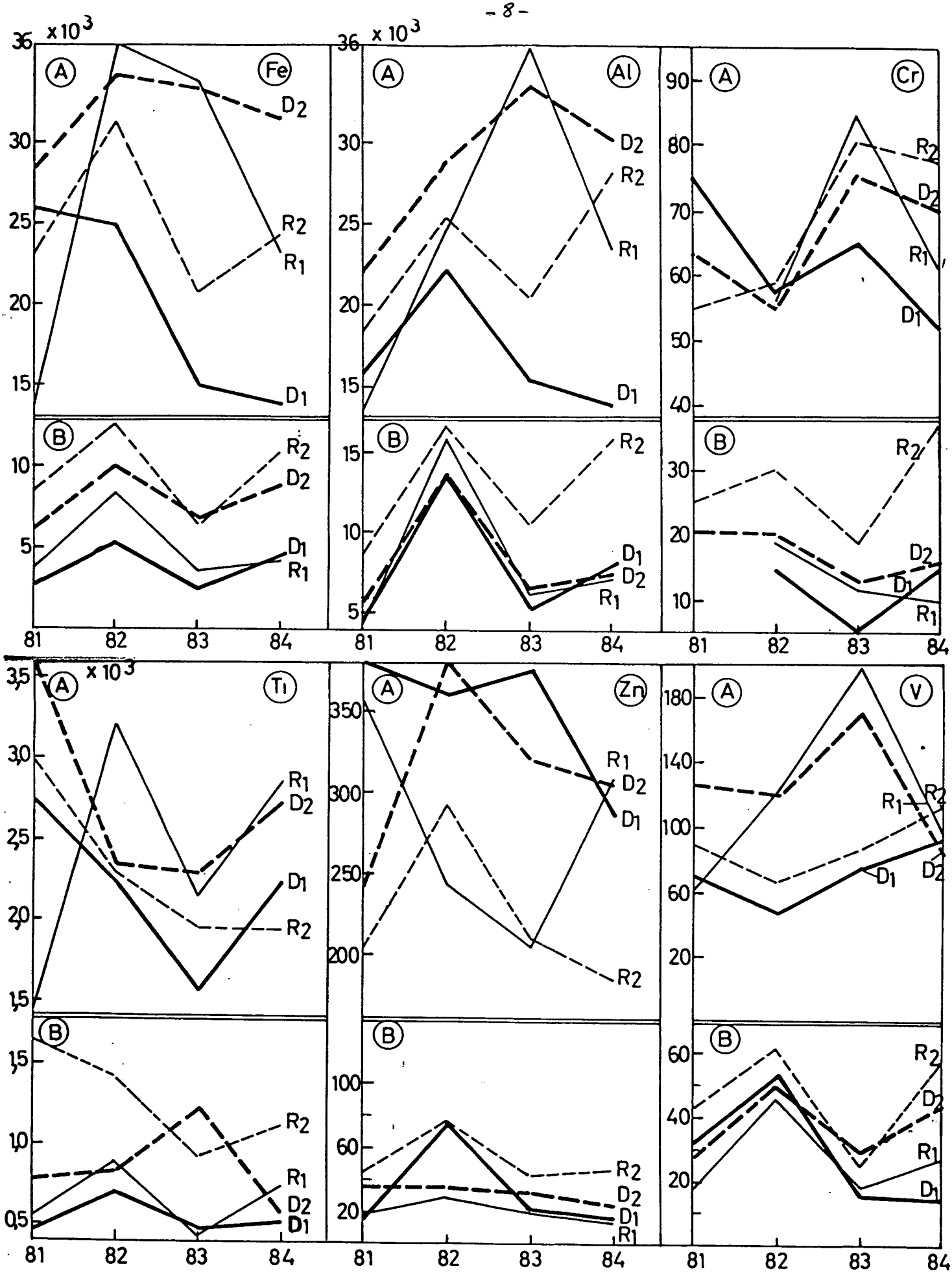

Figure 3 - Evolution of the concentration of heavy metals in sediments
A : < 63 µm ; B : < 500 µm

Table 2 - Heavy metal concentrations (mg/kg) in the sediment fractions, average and relative standard deviation

Area	Fe		Al		Cr		Ti		Zn		V	
	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm
D1	20 064	3 711	16 460	8 010	62	10	2 185	538	358	32	72	29
	(20)	(18)	(44)	(26)	(26)	(28)	(25)	(21)	(30)	(53)	(29)	(15)
D2	31 841	7 962	23 169	8 496	66	17	2 807	843	337	31	125	38
	(17)	(19)	(24)	(28)	(36)	(35)	(36)	(38)	(64)	(39)	(57)	(34)
R1	27 405	5 055	24 194	8 791	68	13	2 413	650	278	21	122	27
	(19)	(22)	(47)	(29)	(19)	(40)	(38)	(47)	(49)	(43)	(56)	(24)
R2	24 912	9 663	23 101	13 079	69	27	2 305	1 268	223	52	90	47
	(16)	(35)	(45)	(52)	(31)	(45)	(20)	(50)	(64)	(75)	(45)	(55)

In the period 1976-80 the so-called "total extraction" of metals was performed with 5M nitric acid (Baeteman et al. 1982). Although the data cannot be compared directly, no evidence of accumulation of heavy metals due to the discharges of titanium dioxide waste could be noted.

The above results based on total destruction of the sediment with hydrofluoric acid confirm these findings.

3.2.2. Extraction with acetic acid.

The average fractions of heavy metals extracted, calculated as a percentage of the total metal content are reported in table 3. There were no significant differences between the four years and hence only the total averages are quoted. Titanium values were below the detection limit of 10 mg/kg. This was also the case for aluminium in the $< 500\ \mu m$-fraction (detection limit 125 mg/kg).

With a few exceptions, the extractable fractions were comparable for the $< 63\ \mu m$ samples again indicating that the dumping of titanium dioxide waste did not influence the availability of metals in the mud fraction. The results of the $< 500\ \mu m$ samples in the D1 area were clearly lower than in the other areas, area R2 showing the highest values. This stresses again the influence of coastal pollution.

The figures reported here are in good agreement with those quoted for rather similar sediments in France (Joanny et al. 1981).

The question of to what extent the concentrations of a particular contaminant found in a sediment can be considered to represent the fraction potentially available to organisms living in or on this sediment is still a matter for research (ICES 1983, 1987). Whatsoever, it is clear that the metal concentration of this fraction did not increase significantly by the dumping of titanium dioxide waste off the Belgian coast.

3.3. Biota.

Results are reported in tables 4 and 5.

In benthic organisms, titanium was also determined but the data appeared afterwards to be unreliable due to a severe interference by calcium ; they were deleted.

For both epibenthos and fish no clear temporal nor spatial differences in the concentrations of heavy metals were noted so that no evidence of accumulation of metals in marine biota due to the dumpings of titanium dioxide waste could be shown. This was also observed in the previous work (Baeteman et al. 1982). Furthermore the data were within the same ranges of values found in other parts of the Southern North Sea (De Clerck et al. 1979, 1984 ; Vyncke et al. 1981 ; Guns et al. 1984 ; Vos et al. 1986).

In and around a Dutch disposal site, no significant differences in heavy metal content could be detected in hermit crab, sea star, flounder and plaice (Spaans 1985). In a more critical area, the German Bight, increased heavy metal concentrations have been recorded in the epidermal tissues of dab (Limanda limanda)

Table 3 - Fractions of heavy metals extracted with 25 % acetic acid (calculated as percentages of the total metal content).

Area	Fe		Al		Cr		Zn		V	
	< 63 µm	<500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm	< 63 µm	< 500 µm
D1	11,4	5,4	3,7	-	21,0	5,0	86,3	10,0	34,7	5,8
D2	11,8	8,9	2,2	-	22,7	10,6	76,3	25,2	19,0	18,7
R1	10,3	8,7	1,7	-	14,7	10,0	87,1	23,8	15,6	20,0
R2	14,4	13,3	1,7	-	21,7	11,8	79,8	44,2	26,7	21,7
Mean	12,0	9,1	2,3	-	20,0	9,4	82,4	25,8	24,0	16,6

Table 4 - Heavy metal content of epibenthos (mg/kg) in TiO_2-dumping areas (D1 and D2) and in reference zones (R1 and R2)

	D1					D2					R1					R2				
	81	82	83	84	Mean	81	82	83	84	Mean	81	82	83	84	Mean	81	82	83	84	Mean
										Hg										
Sea star	0,07	0,08	0,08	-	*0,08*	0,13	0,14	0,10	0,11	*0,12*	0,09	0,11	0,07	0,11	*0,09*	0,06	0,08	0,05	-	*0,06*
Hermit crab	0,06	0,04	0,03	-	*0,04*	0,07	0,07	0,06	0,06	*0,07*	0,11	0,05	0,04	0,05	*0,06*	0,06	0,06	-	0,02	*0,05*
Swimming crab	0,02	-	0,06	-	*0,04*	0,07	0,07	0,04	0,07	*0,06*	0,04	0,08	0,02	0,04	*0,04*	0,03	0,07	0,03	0,03	*0,04*
Brittle star	0,04	0,07	0,05	-	*0,06*	0,07	0,07	0,04	0,03	*0,05*	0,04	0,06	0,03	0,03	*0,04*	-	0,04	0,03	0,01	*0,03*
										Cd										
Sea star	0,21	0,30	0,13	-	*0,21*	0,27	0,45	0,16	0,39	*0,32*	0,15	0,28	0,11	0,33	*0,22*	0,14	0,31	0,08	-	*0,18*
Hermit crab	0,40	0,15	0,07	-	*0,21*	0,21	0,12	0,10	0,17	*0,15*	0,27	0,21	0,11	0,09	*0,17*	0,20	0,15	-	0,16	*0,17*
Swimming crab	0,25	-	0,03	-	*0,14*	0,14	0,13	0,07	0,05	*0,10*	0,17	0,11	0,02	0,06	*0,09*	0,14	0,12	0,02	0,07	*0,09*
Brittle star	0,12	0,23	0,09	-	*0,15*	0,15	0,22	0,09	0,08	*0,14*	0,15	0,20	0,09	0,08	*0,13*	-	0,22	0,10	0,07	*0,13*
										Pb										
Sea star	0,14	0,60	0,92	-	*0,55*	0,80	1,79	1,23	2,22	*1,51*	0,48	0,32	0,55	0,32	*0,42*	0,39	1,43	0,74	-	*0,85*
Hermit crab	0,07	0,29	0,29	-	*0,22*	0,13	1,34	0,40	0,47	*0,59*	0,07	0,25	0,40	0,61	*0,33*	0,15	0,82	-	0,50	*0,49*
Swimming crab	0,20	-	0,58	-	*0,39*	0,07	1,52	0,36	0,37	*0,58*	0,11	0,30	1,79	0,29	*0,62*	0,10	0,85	0,30	1,13	*0,60*
Brittle star	0,85	0,25	0,30	-	*0,47*	0,89	1,35	0,30	0,20	*0,69*	0,07	1,85	0,12	0,11	*0,54*	-	0,21	0,02	0,08	*0,10*
										Fe										
Sea star	15,3	-	18,3	-	*16,8*	43,9	-	52,6	84,1	*60,2*	48,1	-	16,0	175	*79,7*	36,6	-	33,3	-	*34,9*
Hermit crab	29,2	-	104	-	*66,4*	64,7	-	123,8	73,6	*87,4*	39,6	-	78,8	150	*89,5*	102,0	-	-	100,2	*101*
Swimming crab	25,7	-	23,4	-	*24,6*	24,3	-	43,7	61,1	*43,0*	27,2	-	31,8	36,6	*31,9*	23,9	-	48,1	103,1	*58,3*
Brittle star	1,0	-	17,7	-	*9,4*	1,7	-	29,5	2,5	*11,2*	1,0	-	6,0	1,3	*2,8*	-	-	8,7	10,9	*9,8*
										Cu										
Sea star	2,4	3,0	4,2	-	*3,2*	3,1	3,8	2,9	3,3	*3,3*	2,4	2,6	2,6	3,1	*2,7*	3,0	3,3	3,3	-	*3,2*
Hermit crab	29,6	21,2	25,8	-	*25,5*	25,3	27,8	24,3	24,1	*25,4*	25,2	33,2	20,5	22,1	*25,3*	31,0	23,6	-	23,6	*26,1*
Swimming crab	20,0	-	7,2	-	*13,6*	7,9	8,4	8,4	9,5	*8,6*	9,0	7,7	5,0	6,6	*7,1*	8,2	5,8	7,6	7,3	*7,2*
Brittle star	2,5	2,4	2,5	-	*2,5*	2,6	3,1	2,3	2,7	*2,7*	2,4	3,0	2,5	2,7	*2,7*	-	3,1	2,3	2,5	*2,6*
										Zn										
Sea star	21,7	54,4	57,4	-	*44,5*	59,8	82,60	45,8	52,6	*60,2*	54,1	53,1	28,6	56,4	*48,1*	27,5	75,0	32,3	-	*44,9*
Hermit crab	25,4	28,5	30,6	-	*28,2*	25,6	36,3	29,7	40,5	*33,0*	23,3	30,1	33,8	32,0	*29,8*	30,5	33,8	-	32,6	*32,3*
Swimming crab	35,1	-	27,4	-	*31,2*	16,4	28,7	23,1	19,9	*22,0*	19,8	25,0	25,5	25,6	*24,0*	23,4	26,8	22,8	34,2	*26,8*
Brittle star	30,0	-	30,0	-	*30,0*	54,4	74,4	31,2	30,2	*47,6*	54,6	55,8	47,8	30,7	*47,2*	-	50,8	40,5	23,2	*38,2*
										Cr										
Sea star	0,26	0,12	0,09	-	*0,16*	0,29	0,26	0,19	0,17	*0,23*	0,31	0,33	0,05	0,28	*0,24*	0,24	0,28	0,13	-	*0,22*
Hermit crab	0,02	0,15	0,29	-	*0,15*	0,10	0,34	0,28	0,16	*0,22*	0,03	0,30	0,16	0,21	*0,18*	0,04	0,57	-	0,25	*0,29*
Swimming crab	0,07	-	0,12	-	*0,10*	0,01	0,34	0,20	0,13	*0,17*	0,13	0,28	0,16	0,13	*0,18*	0,13	0,41	0,10	0,26	*0,23*
Brittle star	0,06	0,03	0,08	-	*0,06*	0,05	0,05	0,03	0,03	*0,04*	0,05	0,09	0,01	0,03	*0,05*	-	0,03	0,01	0,01	*0,02*
										Ni										
Sea star	0,40	0,30	0,13	-	*0,28*	0,20	0,31	0,28	0,16	*0,24*	0,20	0,27	0,12	0,25	*0,21*	0,20	0,33	0,17	-	*0,23*
Hermit crab	0,20	0,66	0,24	-	*0,37*	0,20	0,32	0,27	0,27	*0,27*	0,20	0,35	0,50	0,16	*0,30*	0,10	0,31	-	0,30	*0,24*
Swimming crab	0,10	-	0,25	-	*0,18*	0,20	0,32	0,29	0,16	*0,24*	0,20	0,31	0,12	0,12	*0,19*	0,10	0,35	0,22	0,41	*0,27*
Brittle star	0,20	0,53	0,12	-	*0,28*	0,30	0,45	0,24	0,20	*0,30*	0,10	0,38	0,25	0,12	*0,21*	-	0,33	0,24	0,12	*0,23*

Table 5 - Heavy metal content of shrimp and fish (mg/kg)(1982)

	D1	D2	R1	R2
		Hg		
Shrimp	-	0,07	0,07	0,06
Plaice	0.03	0,07	0,16	0,09
Flounder	0,19	0,34	0,18	0,22
Whiting	0,09	0,09	0,13	0,12
Cod	0,10	0,11	0,14	0,15
		Cd		
Shrimp	-	0,014	0,013	0,012
Plaice	0,009	< 0,005	< 0,005	0,009
Flounder	< 0,005	< 0,005	< 0,005	< 0,005
Whiting	0,008	0,008	< 0,005	< 0,005
Cod	< 0,005	< 0,005	0,006	< 0,005
		Pb		
Shrimp	-	0,15	0,58	0,17
Plaice	0,09	0,08	0,07	0,08
Flounder	0,06	0,07	0,07	0,07
Whiting	0,06	0,08	0,06	0,07
Cod	0,05	0,07	0,05	0,09
		Fe		
Shrimp	-	37,5	111,6	35,8
Plaice	1,6	2,2	2,7	3,0
Flounder	1,8	2,5	2,6	3,2
Whiting	1,3	1,2	0,8	1,6
Cod	7,3	3,9	7,8	8,3
		Cu		
Shrimp	-	11,1	14,4	10,9
Plaice	0,6	0,5	0,5	0,5
Flounder	0,5	0,5	0,5	0,6
Whiting	0,5	0,5	0,7	0,6
Cod	0,5	0,4	0,4	0,5
		Zn		
Shrimp	-	29,5	29,3	26,5
Plaice	9,0	7,7	10,1	10,6
Flounder	7,9	11,6	11,3	17,1
Whiting	4,6	5,2	4,6	5,9
Cod	5,0	5,2	5,2	5,9
		Cr		
Shrimp	-	0,40	0,17	0,31
Plaice	0,40	0,34	0,50	0,42
Flounder	0,18	0,27	0,16	0,28
Whiting	0,34	0,44	0,31	0,36
Cod	0,20	0,19	0,20	0,44
		Ni		
Shrimp	-	0,29	0,18	0,17
Plaice	0,13	0,17	0,17	0,16
Flounder	0,15	0,20	0,11	0,13
Whiting	0,15	0,20	0,14	0,17
Cod	0,07	0,11	0,17	0,12
		Ti		
Shrimp	-	3,18	< 0,05	2,83
Plaice	< 0,05	< 0,05	0,13	< 0,05
Flounder	0,23	< 0,05	0,08	0,16
Whiting	0,10	< 0,05	< 0,05	0,07
Cod	0,25	0,11	< 0,05	0,07

together with increased prevalences of epidermal papilloma There are indications that titanium dioxide waste is at least partially responsible for this situation (Dethlefsen 1985).

4. CONCLUSIONS

The dumping of about 12 million tons of titanium dioxide waste over a period of 25 years in a rather restricted area off the Belgian coast did not have any apparent influence on the heavy metal content of the water, sediments and biota. This confirms the view of ICES (1984) that when the hydrodynamic pattern of the dumping site guarantees a thorough mixing and rapid dilution, no accumulation of heavy metals is to be expected. In this respect it should be recalled that the average flushing time of the North Sea is two years. Nevertheless it cannot be overlooked that large amounts of heavy metals are entering the marine environment due to the discharges of titanium dioxide waste, not only from Belgium but also from other North Sea riparian countries.

Heavy metals associated with particulate matter can be carried over large distances and be deposited in areas where conditions for sedimentation are more favourable e.g. the German Bight and the Norwegian Trench, thus contributing significantly to the heavy metal load in those areas (Carlson 1986).

In accordance with the EEC-directive (1978), Belgium will ban all dumpings of titanium dioxide wastes from the 1st January 1990 on (Royal Decree of 23 January 1987). This decision has been made taking also into account the fact that new titanium dioxide production processes are now available which eliminate most of the waste.

ACKNOWLEDGMENT

Part of this work was carried out with ships made available by the Ministry of Public Health and Environment, North Sea Mathematical Models Management Unit, Brussels.

REFERENCES

- AMBIO S.A. (1987) : Environmental impact assessment of dumping titanium dioxide wastes in the Gulf of Cadiz of Tioxide Espana, S.A., Standing Advisory Committee on Scientific Advice, paper 14/10/1-E, Oslo Commission, London.
- APHA (1976) : Standard Methods for the Examination of Water and Waste Water, 14th Ed., American Public Health Association, Washington D.C., p. 440.
- BAETEMAN, M., GABRIELS, R. and GUNS, M. (1982) : Report n° 185 of the Fisheries Research Station, Oostende (in Dutch).
- CARLSON, H. (Ed). (1986) : Quality Status of the North Sea, A report prepared for the International Conference on the protection of the North Sea, Bremen 1984, Deutsche Hydrographische Zeitschrift, Ergänzungsheft Reihe 8, Nr. 16, p. 7.

- DE CLERCK, R., VANDERSTAPPEN, R., VYNCKE, W. and VAN HOEYWEGHEN, P. (1979) : La teneur en métaux lourds dans les orgnaismes marins provenant de la capture accessoire de la pêche côtière belge, Revue de l'Agriculture 32, 793-801.

- DE CLERCK, R., GUNS, M., VYNCKE, W. and VAN HOEYWEGHEN, P. (1984) : La teneur en métaux lourds dans le cabillaud, le flet et la crevette des eaux côtières belges, Revue de l'Agriculture, 37, 1079-1086.

- DETHLEFSEN, V. and VON WESTERNHAGEN, H. (1983) : Oxygen deficiency and effects on bottom fauna in the Eastern German Bight 1982, Meeresforschung 30, 42-53.

- DETHLEFSEN, V. (1985) : Review of the effects of dumping of wastes from titanium dioxide production in the German Bight, Marine Environmental Quality Committee C.M. 1985/E:2, International Council for the Exploration of the Sea, Copenhagen.

- DEUTSCHES HYDROGRAPHISCHES INSTITUT (1984) : Ueberwachung des Meeres - Bericht für das Jaar 1983, pp. 1-30.

- EEC (1978) : Council Directive on the dumping of wastes from the titanium dioxide industry (78/176/EEC), Official Journal of the European Communities, 25 Feb. 78, N° L 54/19.

- EEC (1982) : Council Directive on procedures for the surveillance and monitoring of environments affected by waste from the titanium dioxide industry (82/883/EEC), Official Journal of the European Communities, 31 Dec. 82, N° L 378/1.

- GABRIELS, R. (1973) : Analysis of horticultural crops, soil mixes and irrigation waters by flame emission and atomic absorption spectrometry, 4th Int. Conf. on Atomic Spectroscopy and 20th Canadian Spectroscopy Symposium, Toronto.

- GABRIELS, R., VAN KEIRSBULCK, W. and ENGELS, E. (1981) : Spectrofluorimetric determination of aluminium in plants, soils and irrigation waters, Laboratory Practice 30 (2), 122-123.

- GABRIELS, R., VAN KEIRSBULCK, W. and ENGELS, E. (1983) : Spectrophotometric determination of titanium in plants, soils and irrigation waters, Laboratory Practice 32 (5), 93-94.

- GUNS, M., DE CLERCK, R., VYNCKE, W. and VAN HOEYWEGHEN, P. (1984) : Poursuite de l'étude de la teneur en métaux lourds dans les organismes marins de la Mer du Nord, Revue de l'Agriculture 37, 311-318.

- ICES (1983) : Report of the ICES Advisory Committee on Marine Pollution 1983, Cooperative Research Report N° 124, International Council for the Exploration of the Sea, Copenhagen.

- ICES (1984) : Report of the ICES Advisory Committee on Marine Pollution 1984, Cooperative Research Report N° 132, International Council for the Exploration of the Sea, Copenhagen.

- ICES (1987) : Report of the ICES Advisory Committee on Marine Pollution 1986, Cooperative Research Report N° 142, International Council for the Exploration of the Sea, Copenhagen.

- JOANNY, M., CHAUSSEPIED, M. and CORRE, F. (1981) : Métaux-traces dans les sédiments marins, Intercalibration 1980, Joint Monitoring Group, paper VI/7/10-F, Oslo and Paris Commissions, London.

- KNUTZEN, J. (1983) : A review of the effects on aquatic ecosystems of acid iron waste from the production of titanium dioxide by the sulphate process, NIVA Report n° 0-82012, Norwegian Institute for Water Research, Royal Norwegian Council for Scientific and Industrial Research, Oslo.

- MOMMAERTS, J.P. and D'HONDT, P. (1986) : Evaluation de l'impact sur l'environnement marin de l'immersion en mer de déchets de production de l'industrie du dioxyde de titane par les firmes NL Chemicals et Bayer Antwerpen, Ministère de la Santé Publique, Unité de Gestion du Modèle Mathématique de la Mer du Nord et de l'Estuaire de l'Escaut, Brussels.

- OSLO COMMISSION (1985a) : Code of Practice for the dumping of acid wastes from the TiO_2 industry at sea, in : First to Fourth Annual Reports, Oslo Commission, London pp. 55-64.

- OSLO COMMISSION (1985b) : Monitoring of sea areas where titanium dioxide wastes are dumped, in : Fifth annual Report, Oslo Commission, London, pp. 103-105.

- ROEKENS, E. and VAN GRIEKEN, R. (1983) : Effects of titanium dioxide industry waste dumping on sea water chemistry, Water Research 17, 1385-1392.

- SCHMIDT, D. (1980) : Comparison of trace heavy-metal levels from monitoring in the German Bight and the South-Western Baltic Sea, Helgoländer Meeresuntersuchungen 33, 576-586.

- SPAANS, L. (1985) : Monitoring the environmental effects of dumping of TiO_2-wastes into the North Sea, Joint Monitoring Group, paper 10/8/2-E, Oslo and Paris Commissions, London.

- STOOCKEY, L. (1970) : Ferrozine - A nex spectrophotometric reagent for iron, Analytical Chemistry 42, 779.

- VACCARO, R., GRICE, G., ROVE, G. and WIEBE, P. (1972) : Acid iron waste disposal and the summer distribution of standing crops in the New York Bight, Water Research 6, 231-256.

- VANDAMME, K. and GABRIELS, R. (1983) : Analyse physico-chimique des sédiments dans les lieux de déversements des déchets industriels de la zone côtière belge, Revue de l'Agriculture 36, 1523-1533.

- VANDERSTAPPEN, R., DE CLERCK, R., VYNCKE, W. and MOERMAN, R. (1978) : Les teneurs en mercure, zinc, cuivre, plomb et cadmium dans le hareng, Revue de l'Agriculture 32, 331-336.

- VOS, G., HOVENS, J. and HAGEL, P. (1986) : Chromium, nickel, copper, zinc, arsenic, selenium, cadmium, mercury and lead in Dutch fishery products 1977-1984, The Science of the Total Environment 52, 25-40.

- VYNCKE, W., VANDERSTAPPEN, R., DE CLERCK, R., MOERMANS, R. and VAN HOEYWEGHEN, P. (1981) : L'évolution de la teneur en métaux lourds dans la plie, le merlan, le sprat et les crevettes pêchés dans les eaux côtières belges, Revue de l'Agriculture 34, 1351-1365.

- WALL, G., WILDING, L. and GMECK, N. (1978) : Journal of Environmental Quality 7, 319-325.

- WEICHART, G. (1975) : Untersuchungen über die Fe-Konzentration im Wasser der Deutschen Bucht im Zusammenhang mit dem Einbringen von Abwässern aus der Titandioxid-Produktion, Deutsche Hydrographische Zeitschrift 28, 49-61.

- WEICHART, G. (1977) : Untersuchungen über die Verdünnung von Abwässern aus der Titandioxid-Produktion bei Einleitung in das Schaubenwasser eines Schiffes, Deutsche Hydrographische Zeitschrift 30, 37-50.