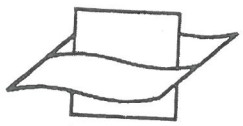
Trace metals in the Belgian dumping area for acid wastes from the titanium dioxide industry (1985-89)



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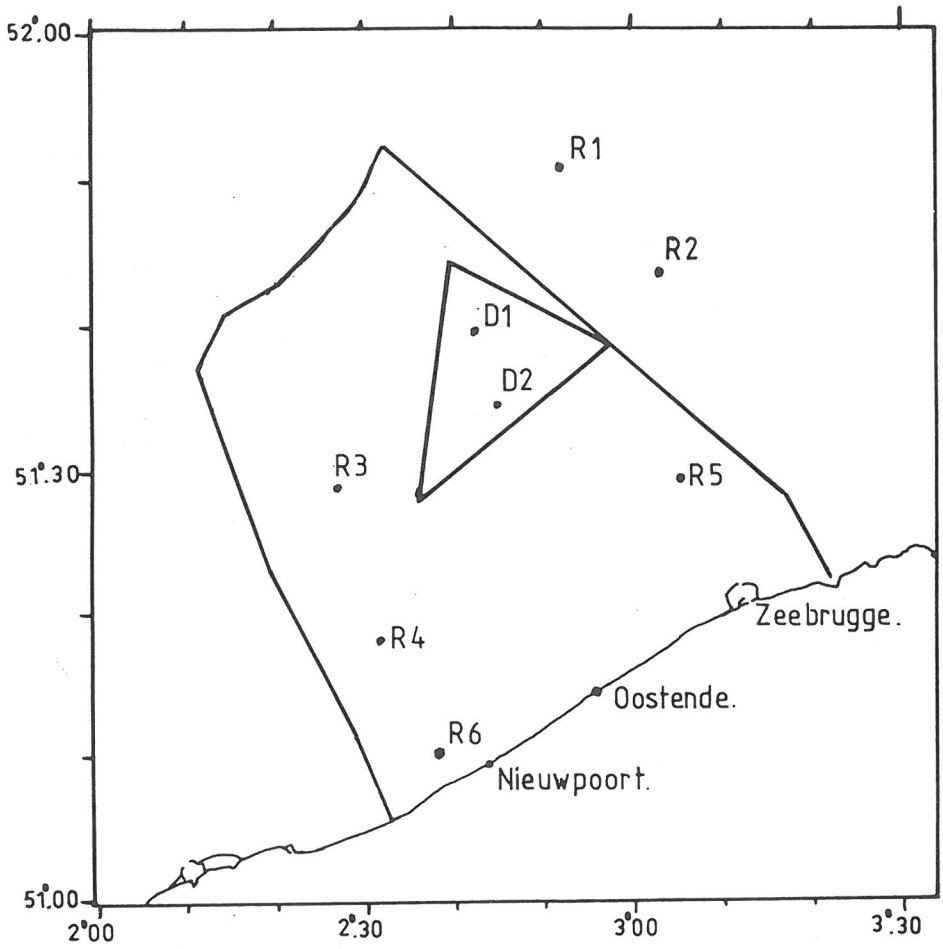
Summary
During the period of investigation, two stations in the dumping site and six reference stations were monitored.
In water and sediments only the iron content, a key parameter, was determined. In benthos, Fe, Cr, Ni, Zn, Pb, Cu and Cd were assessed.
The iron content was very similar in both the dumping area and in five reference stations (0.06-0.08 mg/l). In the station nearest to the coast however, the concentrations were 2 to 3 times higher, showing the influence of river inputs. There was no temporal trend.
A lack of dissolved oxygen was never observed and no marked differences between the eight areas were noted indicating that the oxidation of Fe^{++}, the main component of the waste stream, had no measurable consequences in the water column.
Abnormally low pH-values were not observed.
In the sediments, no temporal trend in iron concentrations could be detected. No higher amounts were noted in the dumping area. The concentration of iron 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 iron content in the total mud fraction ($< 63\ \mu m$) decreased seawards (from ca 4.2 to 0.12 g/kg) up to about 20 nautical miles.
In sea star (*Asterias rubens*), hermit crab (*Pagurus bernhardus*), swimming crab (*Macropipus holsatus*) brittle star (*Ophiura texturata*) and cut trough shell (*Spisula subtruncata*), there was neither a clear temporal trend nor evidence of accumulation of metals due to the dumping of titanium dioxide waste.
Nevertheless, large amounts of heavy metals associated with particulate matter can be carried over long distances before being deposited. For this reason, all dumpings were banned since 1990.

1. Introduction

The discharge of waste from the titanium dioxide industry off the Belgian coast began in 1961 and lasted until the end of 1989, when Belgium banned all dumping activities. Monitoring of the discharge sites started in 1976 and two reports on the levels of heavy metals in water, sediments and biota covering the period 1976-1984 were published. No detrimental effects to the marine environment were assessed (Baeteman et al., 1982, 1987).

In 1985, a new area in the Northern part of the Belgian continental shelf was designated by the Ministry of the Environment (fig.1). In 1985-1988 an average of 600.000 t per year was discharged by two factories. In 1989, amounts were gradually decreased and dumping was ceased in December.
The average main composition of the waste was 20 % sulphuric acid, 2 % iron, 0.3 % aluminium, 0.2 % titanium, 450 ppm vanadium and 170 ppm chromium. Other trace elements such as zinc, copper, lead and

Figure 1 **Location of the sampling stations**



D = dumping station
R = reference station
(triangle : dumping area)

nickel occurred at levels not exceeding 5 ppm.

This paper reports the results of investigations carried out during 1985-89 on water, sediments and benthic organisms in the dumping site (2 stations) and in six reference stations (fig. 1). In water and sediments only the iron content, which is a key parameter, was determined. In benthos, other trace metals were also assessed.

In the same period a biological monitoring programme was also carried out on the eight stations. The results of the latter will be published separately.

2. Materials and methods

2.1. Water

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

2.2. Sediments

Samples were taken with a Van Veen-grab once a year in each station. They were kept

at -28°C until analysis. The < 63 μm fraction was separated in a first sub-sample by wet sieving. The average percentages of this fraction in the sediment are reported in table 2. In a second sub-sample, particles larger than 500 μm were removed (maximum 5 %). The latter could thus be regarded as representing the total sediment.
For the extraction of the total iron 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. Determination was carried out by atomic absorption spectrometry.

2.3. Biota

Sea star (*Asterias rubens*), hermit crab (*Pagurus bernhardus*), swimming crab (*Macropipus holsatus*), brittle star (*Ophiura texturata*) and cut trough shell (*Spisula subtruncata*) were collected once a year. Bulked samples of 6 to 10 animals were taken for analysis.
All samples were kept at −28°C prior to analysis.
The organisms were finely chopped and analysed completely, the shells of hermit crab and trough shell having been removed beforehand.
Analyses of Fe, Cr, Ni, Zn, Pb, Cu, Cd were carried out with atomic absorption spectrometry after digestion of the ashed samples with concentrated nitric acid and hydrogen peroxide.
Mercury was determined by cold vapour atomic absorption spectrometry after digestion of the fresh samples with sulphuric acid and hydrogen peroxide (De Clerck et al., 1988).

3. Results and discussion

3.1. Water

Average results are reported in table 1.
The iron content was very similar in both the dumping area and in reference stations 1-5 (0.06-0.08 mg/l). In the coastal station R6 however, the concentrations were 2 to 3 times higher, showing the influence of river inputs. There was no temporal trend. This was also observed during the previous investigations (Baeteman et al., 1987). 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 (Van Zwol and Bos, 1990). 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 (Schmidt, 1980; Tiews, 1989).
A lack of dissolved oxygen was never observed and no marked differences between the eight areas were noted indicating that the oxidation of Fe++, the main component of the waste stream, had no measurable consequences in the water column. This was also the case in and around a titanium dioxide dumping site in the German Bight for the period 1987-89 (Anon., 1991).
Abnormally low pH-values were not noted. It has been shown repeatedly that a short time after discharge, pH-values become normal again (Roekens and Van Grieken, 1983).
In the two dumping stations and in reference stations 1-5 mean pH-values were between 8.0 and 8.3. In the coastal station R6 however the values were 0.1 - 0.3 units lower, again indicating the influence of land-based pollution sources. The same results were obtained in the German Bight in 1987-89 (Anon., 1991).

3.2. Sediments

From the results shown in table 2 it appears that neither for the < 500 μm nor for the < 63 μm fraction a temporal trend in iron concentration could be detected. No higher amounts were noted in the dumping area. As already found during the previous investigations (Baeteman et al., 1987) the concentration of iron (and other 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. From table 2 it is apparent that the < 500 μm fraction showed a seaward decreasing gradient especially in stations R4, R5 and R6 which stopped about 20 nautical miles from the coast. The evolution of the average concentrations in the mud fraction was quite similar. When taking into account the percentage of the < 63 μm fraction however, another picture emerges.
Fig. 2 shows the total iron loads of the < 63 μm and 63-500 μm fractions respectively for the eight stations. The total iron content per kg sediment of the < 63μm fraction was calculated by multiplying the iron concentration in this fraction by the percentage of it

Table 1 **Iron (mg/l), dissolved oxygen concentrations (mg/l) and pH in sea water**

Station	Year	Fe	O_2	pH
Dumping 1	85	0,050	9.0	8.3
	86	0.035	7.8	8.0
	87	0.076	7.9	8.0
	88	0.052	8.3	8.2
	89	0.030	9.1	8.1
	Av.	0.048	8.4	8.1
Dumping 2	85	0.042	9.1	8.3
	86	0.046	7.9	8.1
	87	0.065	8.1	8.2
	88	0.063	8.3	8.1
	89	0.050	9.4	8.1
	Av.	0.053	8.6	8.1
Ref. 1	85	0.025	9.0	8.3
	86	0.031	8.1	8.1
	87	0.070	8.0	8.2
	88	0.023	8.4	8.2
	89	0.025	9.1	8.1
	Av.	0.035	8.5	8.2
Ref. 2	85	0.051	9.2	8.3
	86	0.045	8.1	8.1
	87	0.072	7.9	8.2
	88	0.050	8.4	8.1
	89	0.055	9.4	8.0
	Av.	0.054	8.6	8.1
Ref. 3	85	0.023	8.9	8.2
	86	0.036	8.9	8.2
	87	0.070	8.0	8.2
	88	0.053	8.4	8.1
	89	0.062	9.1	8.0
	Av.	0.049	8.5	8.1
Ref. 4	85	0.025	9.3	8.3
	86	0.064	8.0	8.0
	87	0.075	7.9	8.2
	88	0.052	8.2	8.0
	89	0.042	9.1	8.1
	Av.	0.052	8.5	8.1
Ref. 5	85	0.073	9.1	8.3
	86	0.052	7.9	8.1
	87	0.022	8.1	8.0
	88	0.025	8.2	8.0
	89	0.037	9.2	8.1
	Av.	0.042	8.5	8.1
Ref. 6	85	0.139	9.3	8.0
	86	0.070	7.9	8.0
	87	0.090	7.7	7.8
	88	0.190	8.3	7.8
	89	0.145	8.9	7.9
	Av.	0.127	8.4	7.9

Table 2 Concentration of iron in sediments (g/kg dry weight)

Station (*)	Year	< 500 µm	< 63 µm
Dumping 1 (1.0 %)	85	2.8	21.7
	86	2.5	21.7
	87	2.1	30.0
	88	2.3	22.7
	89	2.2	19.1
	Av.	2.4	23.0
Dumping 2 (0.6 %)	85	2.2	16.9
	86	2.8	18.8
	87	2.5	20.7
	88	2.5	21.4
	89	2.3	19.5
	Av.	2.5	19.5
Ref. 1 (0.8 %)	85	2.7	24.6
	86	4.0	15.2
	87	3.2	20.2
	88	2.6	23.0
	89	2.1	18.5
	Av.	2.9	20.3
Ref. 2 (0.8 %)	85	3.3	13.0
	86	2.8	18.8
	87	2.6	12.0
	88	2.3	15.4
	89	2.6	16.2
	Av.	2.7	15.1
Ref. 3 (1.1 %)	85	2.7	18.8
	86	3.2	28.1
	87	2.5	31.1
	88	2.8	19.4
	89	3.0	22.4
	Av.	2.8	24.0
Ref. 4 (4.0 %)	85	4.8	21.8
	86	3.6	22.3
	87	3.2	23.8
	88	3.2	23.4
	89	4.0	21.9
	Av.	3.8	22.6
Ref. 5 (6.1 %)	85	4.2	26.1
	86	4.8	26.0
	87	3.4	21.4
	88	4.5	25.6
	89	4.0	24.3
	Av.	4.2	24.6
Ref. 6 (18.0 %)	85	6.2	21.2
	86	6.4	27.5
	87	7.4	18.3
	88	6.5	23.5
	89	7.0	25.6
	Av.	6.7	23.2

(*) average percentage of the < 63 µm fraction in brackets

Table 3 **Trace metals in sea star (mg/kg wet weight)**

Area	Year	Hg	Cd	Pb	Cu	Zn	Ni	Cr	Fe
Dumping 1	85	—	—	—	—	—	—	—	—
	86	0.07	0.098	0.144	3.1	35.5	0.18	0.06	31.0
	87	0.05	0.125	0.157	2.8	29.1	0.08	0.05	15.0
	88	0.02	0.136	0.109	3.0	27.4	0.17	0.05	15.3
	89	0.02	0.137	0.528	3.2	24.7	0.16	0.13	57.4
	Av.	0.04	0.124	0.235	3.0	29.1	0.15	0.07	29.7
Dumping 2	85	—	—	—	—	—	—	—	—
	86	0.07	0.150	0.230	3.0	44.6	0.20	0.07	44.9
	87	—	—	—	—	—	—	—	—
	88	0.02	0.150	0.154	3.1	24.0	0.13	0.05	23.7
	89	0.02	0.197	0.549	2.6	30.0	0.12	0.19	36.5
	Av.	0.04	0.166	0.311	2.9	32.9	0.15	0.10	35.0
Ref. 1	85	—	—	—	—	—	—	—	—
	86	—	—	—	—	—	—	—	—
	87	—	—	—	—	—	—	—	—
	88	0.02	0.126	0.329	3.1	24.5	0.33	0.04	61.2
	89	0.02	0.174	0.171	3.8	28.2	0.15	0.13	52.0
	Av.	0.02	0.150	0.250	3.4	26.4	0.24	0.08	56.6
Ref. 2	85	—	—	—	—	—	—	—	—
	86	0.06	0.086	0.206	3.0	36.6	0.15	0.04	23.5
	87	0.07	0.121	0.374	2.7	27.6	0.06	0.06	31.4
	88	0.04	0.111	0.198	3.0	24.9	0.15	0.04	18.1
	89	0.03	0.170	0.475	3.5	24.0	0.30	0.14	51.8
	Av.	0.05	0.122	0.313	3.1	28.3	0.17	0.07	31.2
Ref. 3	85	—	—	—	—	—	—	—	—
	86	0.08	0.135	0.211	2.8	44.5	0.20	0.07	30.1
	87	—	—	—	—	—	—	—	—
	88	0.02	0.193	0.167	3.3	40.4	0.18	0.03	44.3
	89	0.02	0.247	0.167	2.4	43.7	0.11	0.07	17.3
	Av.	0.04	0.192	0.182	2.8	42.9	0.16	0.06	30.5
Ref. 4	85	—	—	—	—	—	—	—	—
	86	0.07	0.113	0.428	3.2	40.1	0.43	0.16	109.8
	87	0.09	0.130	0.346	3.0	28.2	0.08	0.07	31.0
	88	0.07	0.088	0.283	4.2	33.4	0.32	0.01	21.5
	89	0.06	0.138	0.775	3.6	37.1	0.16	0.15	20.1
	Av.	0.07	0.117	0.458	3.5	34.7	0.25	0.10	45.6
Ref. 5	85	—	—	—	—	—	—	—	—
	86	0.06	0.134	0.614	3.6	30.2	0.15	0.15	85.1
	87	0.08	0.093	0.709	3.2	36.5	0.13	0.13	100.2
	88	0.06	0.110	0.374	3.2	41.7	0.33	0.07	67.0
	89	0.05	0.101	0.261	3.3	34.8	0.17	0.12	43.1
	Av.	0.06	0.110	0.490	3.3	35.8	0.20	0.12	73.9
Ref. 6	85	—	—	—	—	—	—	—	—
	86	—	—	—	—	—	—	—	—
	87	0.07	0.038	0.405	4.5	26.9	0.11	0.05	34.8
	88	0.04	0.035	0.490	3.3	41.3	0.28	0.16	91.2
	89	0.05	0.085	1.566	3.5	72.6	0.63	0.25	48.0
	Av.	0.05	0.053	0.820	3.8	46.9	0.34	0.15	58.0

Table 4 **Trace metals in swimming crab (mg/kg wet weight)**

Area	Year	Hg	Cd	Pb	Cu	Zn	Ni	Cr	Fe
Dumping 1	85	–	–	–	–	–	–	–	–
	86	–	–	–	–	–	–	–	–
	87	0.04	0.035	0.145	6.9	13.7	0.14	0.08	20.8
	88	0.02	0.051	0.081	8.0	16.4	0.19	0.07	40.0
	89	0.03	0.083	0.097	6.7	14.7	0.32	0.12	28.6
	Av.	0.03	0.056	0.108	7.2	14.9	0.22	0.09	29.8
Dumping 2	85	–	–	–	–	–	–	–	–
	86	–	–	–	–	–	–	–	–
	87	–	–	–	–	–	–	–	–
	88	0.02	0.053	0.128	7.6	17.5	0.19	0.07	26.1
	89	0.02	0.067	0.318	7.4	18.9	0.23	0.15	36.7
	Av.	0.02	0.060	0.223	7.5	18.2	0.21	0.11	31.4
Ref. 1	85	0.04	0.052	0.325	6.4	22.7	0.50	0.05	25.0
	86	0.01	0.077	0.147	5.8	25.9	0.22	0.06	26.8
	87	–	–	–	–	–	–	–	–
	88	0.03	0.045	0.078	5.2	19.0	0.26	0.03	37.8
	89	0.03	0.054	0.049	8.8	16.4	0.20	0.05	10.1
	Av.	0.03	0.057	0.150	6.6	21.0	0.30	0.05	24.9
Ref. 2	85	–	–	–	–	–	–	–	–
	86	–	–	–	–	–	–	–	–
	87	0.03	0.053	0.159	5.1	19.6	0.07	0.06	13.4
	88	0.03	0.059	0.083	5.3	18.9	0.15	0.03	16.2
	89	0.03	0.090	0.384	6.8	19.0	0.20	0.10	17.0
	Av.	0.03	0.067	0.208	5.7	19.2	0.14	0.06	15.5
Ref. 3	85	–	–	–	–	–	–	–	–
	86	–	–	–	–	–	–	–	–
	87	–	–	–	–	–	–	–	–
	88	0.02	0.050	0.122	5.4	20.0	0.19	0.04	30.8
	89	0.02	0.081	0.156	12.7	23.6	0.32	0.08	27.7
	Av.	0.02	0.065	0.139	9.1	21.8	0.25	0.06	29.3
Ref. 4	85	–	–	–	–	–	–	–	–
	86	0.07	0.117	0.459	8.2	30.3	0.17	0.20	94.1
	87	0.08	0.061	0.255	6.8	21.5	0.09	0.09	18.2
	88	0.03	0.041	0.139	5.4	15.3	0.23	0.03	27.6
	89	0.05	0.070	0.168	7.6	22.0	0.18	0.14	38.1
	Av.	0.06	0.072	0.255	7.0	22.3	0.17	0.12	44.5
Ref. 5	85	–	–	–	–	–	–	–	–
	86	0.06	0.075	0.893	7.1	24.2	0.39	0.35	227.0
	87	0.08	0.062	0.520	6.9	17.4	0.25	0.27	112.1
	88	0.04	0.048	0.355	6.5	24.3	0.50	0.11	76.0
	89	0.04	0.071	0.850	10.2	32.1	0.95	0.71	267.0
	Av.	0.06	0.064	0.655	7.7	24.5	0.52	0.36	170.5
Ref. 6	85	–	–	–	–	–	–	–	–
	86	0.05	0.075	0.607	5.4	29.4	0.43	0.30	100.2
	87	0.06	0.030	0.637	6.1	19.8	0.18	0.23	65.1
	88	0.03	0.018	0.158	5.0	19.7	0.24	0.20	54.6
	89	0.04	0.058	0.388	6.2	26.5	0.47	0.27	76.0
	Av.	0.05	0.045	0.448	5.7	23.9	0.33	0.25	74.0

Table 5 **Trace metals in hermit crab (mg/kg wet weight)**

Area	Year	Hg	Cd	Pb	Cu	Zn	Ni	Cr	Fe
Dumping 1	85	—	—	—	—	—	—	—	—
	86	0.06	0.073	0.329	17.1	23.8	0.39	0.23	104.8
	87	0.03	0.075	0.400	12.8	25.3	0.17	0.19	90.0
	88	0.03	0.087	0.300	16.4	28.0	0.24	0.13	84.0
	89	0.03	0.207	0.472	25.7	26.1	0.28	0.22	34.2
	Av.	0.04	0.111	0.375	18.0	25.8	0.27	0.19	78.2
Dumping 2	85	—	—	—	—	—	—	—	—
	86	0.04	0.142	0.252	25.3	27.4	0.35	0.19	112.1
	87	—	—	—	—	—	—	—	—
	88	0.03	0.095	0.143	16.1	27.3	0.25	0.15	60.2
	89	0.02	0.127	0.136	22.0	27.8	0.19	0.19	56.0
	Av.	0.03	0.121	0.177	21.0	27.5	0.26	0.18	57.4
Ref. 1	85	0.01	0.074	0.113	15.9	24.8	0.54	0.17	45.1
	86	0.04	0.102	0.174	21.7	23.9	0.37	0.10	73.1
	87	—	—	—	—	—	—	—	—
	88	0.03	0.110	0.150	19.3	30.5	0.47	0.12	79.0
	89	0.02	0.177	0.063	18.5	27.7	0.13	0.12	39.5
	Av.	0.03	0.116	0.125	18.9	26.7	0.38	0.13	59.2
Ref. 2	85	—	—	—	—	—	—	—	—
	86	0.08	0.136	0.386	17.2	24.0	0.33	0.26	136.4
	87	0.04	0.064	0.368	15.6	16.7	0.12	0.13	43.7
	88	0.03	0.096	0.145	20.5	28.5	0.23	0.11	49.5
	89	0.02	0.140	0.138	22.4	29.2	0.23	0.10	22.0
	Av.	0.04	0.109	0.259	18.9	24.6	0.23	0.15	62.9
Ref. 3	85	—	—	—	—	—	—	—	—
	86	0.07	0.276	0.277	32.0	35.6	0.36	0.09	88.4
	87	—	—	—	—	—	—	—	—
	88	0.03	0.092	0.088	16.4	26.0	0.23	0.05	39.9
	89	0.02	0.139	0.206	30.2	24.8	0.33	0.20	88.1
	Av.	0.04	0.168	0.190	26.2	28.8	0.31	0.11	72.1
Ref. 4	85	—	—	—	—	—	—	—	—
	86	0.05	0.144	0.455	16.5	26.2	0.65	0.16	136.3
	87	0.04	0.043	0.301	13.5	24.3	0.13	0.13	65.0
	88	0.02	0.048	0.242	17.4	27.7	0.47	0.18	121.1
	89	0.02	0.075	0.464	22.0	28.5	0.29	0.28	42.3
	Av.	0.04	0.070	0.366	17.4	26.7	0.39	0.19	91.8
Ref. 5	85	—	—	—	—	—	—	—	—
	86	—	—	—	—	—	—	—	—
	87	0.05	0.086	0.498	10.3	23.6	0.13	0.18	104.4
	88	0.02	0.026	0.411	10.5	25.6	0.41	0.21	112.3
	89	0.06	0.183	0.164	14.0	35.0	0.29	0.28	98.1
	Av.	0.04	0.098	0.358	11.6	28.1	0.28	0.22	104.9

Table 6 **Trace metals in brittle star (mg/kg wet weight)** (*)

Area	Year	Hg	Cd	Pb	Cu	Zn	Ni	Cr	Fe
Dumping 1	85	0.03	0.030	0.109	2.3	19.0	0.20	0.05	1.1
	86	0.06	0.045	—	2.8	10.0	0.36	0.03	< 1
	87	0.04	0.022	0.012	1.6	4.0	0.08	0.07	< 1
	88	—	—	—	—	—	—	—	—
	89	0.02	0.085	0.540	3.0	16.0	0.29	0.01	1.4
	Av.	0.04	0.046	0.220	2.4	12.3	0.23	0.04	0.9
Dumping 2	85	0.03	0.035	0.571	3.8	27.5	0.16	0.19	2.1
	86	0.07	0.031	0.020	2.5	1.5	0.24	0.03	< 1
	87	—	—	—	—	—	—	—	—
	88	0.02	0.045	—	2.9	5.4	0.23	0.01	1.2
	89	0.03	0.064	0.057	3.3	8.0	0.24	0.05	1.5
	Av.	0.04	0.044	0.162	3.1	10.6	0.22	0.07	1.3
Ref. 1	85	0.02	0.078	0.016	2.2	20.2	0.24	0.06	1.5
	86	0.09	0.047	0.174	2.8	7.9	0.37	0.01	< 1
	87	—	—	—	—	—	—	—	—
	88	0.03	0.076	0.044	2.9	22.8	0.40	0.02	3.2
	89	0.02	0.078	—	3.3	6.7	0.17	0.04	1.9
	Av.	0.04	0.070	0.078	2.8	14.4	0.30	0.03	1.8
Ref. 2	85	0.04	0.054	0.053	2.5	37.0	0.21	0.05	1.0
	86	0.07	0.017	0.005	2.5	10.3	0.17	0.03	< 1
	87	0.03	0.052	0.034	2.2	14.8	0.07	0.01	< 1
	88	0.03	0.074	0.022	2.9	13.2	0.28	0.01	1.5
	89	0.03	0.083	0.189	3.8	13.3	0.28	0.02	3.7
	Av.	0.04	0.056	0.061	2.8	17.7	0.20	0.03	1.4
Ref. 3	85	0.04	0.033	0.683	5.0	26.9	0.20	0.06	2.3
	86	—	—	—	—	—	—	—	—
	87	—	—	—	—	—	—	—	—
	88	—	—	—	—	—	—	—	—
	89	0.03	0.071	0.376	5.2	36.9	0.42	0.10	2.8
	Av.	0.04	0.052	0.530	5.1	31.9	0.31	0.13	2.5
Ref. 4	85	0.04	0.058	0.044	2.9	27.8	0.27	0.01	1.2
	86	—	—	—	—	—	—	—	—
	87	0.04	0.031	0.030	2.3	11.2	0.07	0.01	< 1
	88	0.03	0.029	—	3.0	6.8	0.37	0.05	1.7
	89	0.03	0.101	0.330	3.3	25.0	0.25	0.05	2.3
	Av.	0.04	0.055	0.135	2.9	17.7	0.24	0.03	1.4
Ref. 5	85	0.03	0.075	0.116	2.9	38.6	0.13	0.01	2.3
	86	0.06	0.096	0.130	3.0	33.9	0.32	0.01	<1
	87	0.04	0.041	0.109	2.1	27.4	0.10	0.01	<1
	88	0.03	0.060	0.064	3.0	25.7	0.56	0.01	1.6
	89	0.02	0.119	0.306	3.8	72.0	0.32	0.14	9.4
	Av.	0.04	0.078	0.145	3.0	39.5	0.29	0.04	2.9
Ref. 6	85	—	—	—	—	—	—	—	—
	86	0.04	0.076	0.059	2.7	29.8	0.37	0.02	<1
	87	0.03	0.038	0.237	2.2	25.4	0.11	0.02	<1
	88	0.02	0.053	0.018	3.1	30.1	0.43	0.01	1.9
	89	0.02	0.078	0.056	3.1	29.1	0.45	0.01	1.0
	Av.	0.03	0.061	0.093	2.8	28.6	0.34	0.023	1.0

(*) For calculating averages. <1 mg/kg was considered to be 0.5 mg/kg

Table 7 **Trace metals in cut trough shell (mg/kg wet weight)**

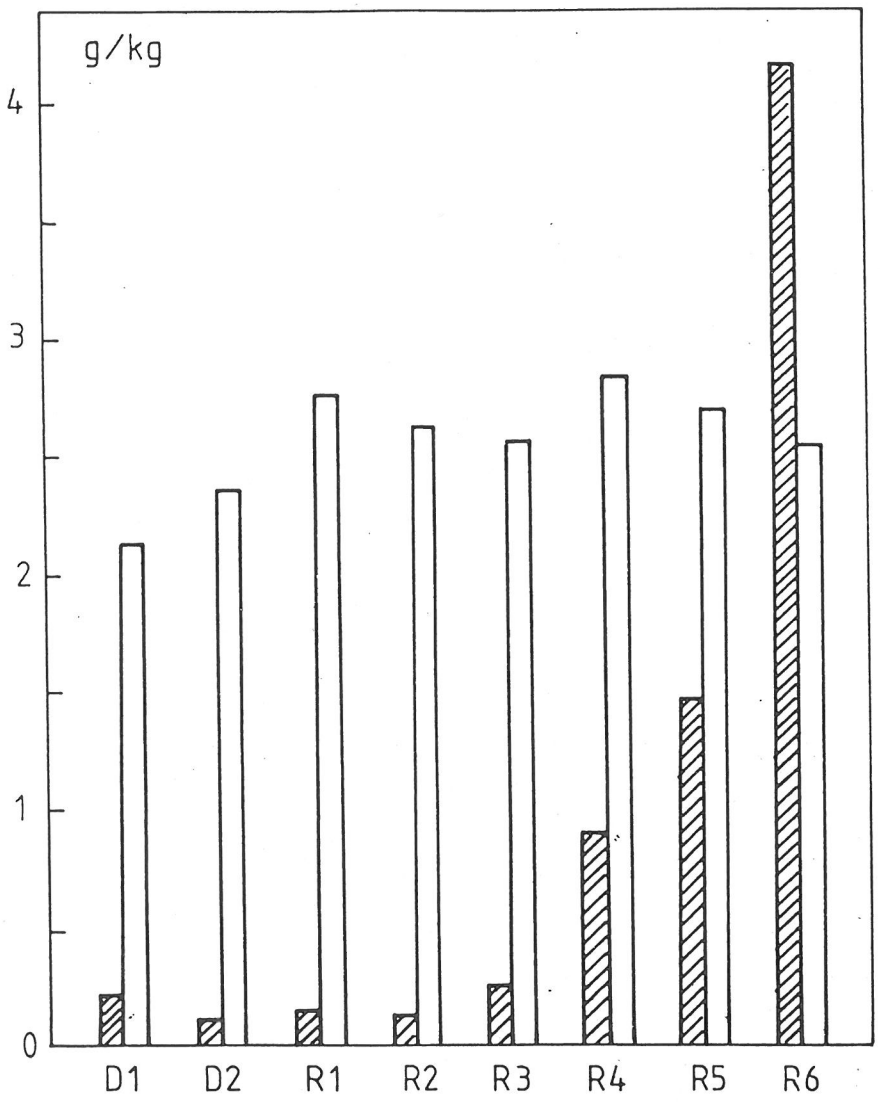
Area	Year	Hg	Cd	Pb	Cu	Zn	Ni	Cr	Fe
Dumping 1	85	0.02	0.103	0.227	3.2	14.0	0.54	0.27	99.4
	86	0.04	0.114	0.143	5.4	17.7	0.39	0.15	79.0
	87	0.03	0.119	0.294	2.5	13.5	0.40	0.53	151.4
	88	0.02	0.110	0.130	1.6	14.2	0.25	0.27	99.9
	89	0.02	0.102	0.124	2.1	12.0	0.30	0.24	62.4
	Av.	0.03	0.110	0.184	3.0	14.3	0.38	0.29	98.4
Dumping 2	85	0.02	0.076	0.171	2.8	11.9	0.52	0.26	149.5
	86	0.06	0.120	0.137	3.5	16.4	0.44	0.18	94.4
	87	—	—	—	—	—	—	—	—
	88	0.02	0.131	0.194	2.1	13.5	0.28	0.45	113.7
	89	0.02	0.116	0.207	2.2	11.7	0.30	0.28	114.0
	Av.	0.03	0.111	0.177	2.7	13.4	0.39	0.29	117.9
Ref. 1	85	0.02	0.093	0.291	4.0	14.5	0.57	0.36	158.2
	86	0.04	0.101	0.280	4.4	19.1	0.77	0.30	153.2
	87	—	—	—	—	—	—	—	—
	88	0.02	0.077	0.170	3.5	18.7	0.51	0.21	82.5
	89	0.02	0.117	0.152	2.2	13.3	0.45	0.37	139.0
	Av.	0.02	0.097	0.223	3.5	16.4	0.58	0.31	133.2
Ref. 2	85	0.03	0.120	0.193	3.9	17.4	0.69	0.45	233.9
	86	—	—	—	—	—	—	—	—
	87	—	—	—	—	—	—	—	—
	88	0.02	0.105	0.135	2.3	11.4	0.29	0.24	56.4
	89	0.01	0.106	0.187	2.0	13.0	0.18	0.34	84.3
	Av.	0.02	0.110	0.172	2.7	13.9	0.39	0.34	124.5
Ref. 3	85	0.02	0.100	0.102	3.2	18.2	0.80	0.36	105.7
	86	—	—	—	—	—	—	—	—
	87	—	—	—	—	—	—	—	—
	88	0.03	0.043	0.113	2.3	14.6	0.57	0.15	89.8
	89	0.01	0.131	0.141	1.4	13.2	0.47	0.20	175.0
	Av.	0.02	0.091	0.119	2.3	15.3	0.61	0.24	123.5
Ref. 4	85	0.02	0.056	0.422	2.2	13.7	0.43	0.27	137.5
	86	0.03	0.109	0.190	3.0	14.5	0.50	0.11	112.2
	87	0.03	0.100	0.328	5.6	12.6	0.40	0.27	147.1
	88	0.02	0.057	0.265	3.2	19.3	0.50	0.33	129.6
	89	0.02	0.123	0.147	3.1	15.2	0.44	0.28	120.0
	Av.	0.02	0.089	0.270	3.4	15.1	0.45	0.25	129.3
Ref. 5	85	0.03	0.050	-	5.2	20.3	0.60	0.62	337.2
	86	—	—	—	—	—	—	—	—
	87	0.04	0.093	0.458	2.4	13.8	0.27	0.41	190.3
	88	—	—	—	—	—	—	—	—
	89	—	—	—	—	—	—	—	—
	Av.	0.03	0.072	0.458	3.8	17.0	0.44	0.51	263.8
Ref. 6	85	—	—	—	—	—	—	—	—
	86	0.03	0.075	0.722	3.4	15.6	0.49	0.45	259.2
	87	—	—	—	—	—	—	—	—
	88	—	—	—	—	—	—	—	—
	89	0.02	0.084	0.911	1.4	23.1	0.99	0.59	264.0
	Av.	0.03	0.080	0.816	2.4	19.4	0.74	0.52	261.6

Table 8 **Average differences in trace metal concentrations (in %) in biota from the Southern area (R4.R5.R6) compared with the Northern area (D1.D2.R1.R2 R3) (*)**

Metal	Sea star	Swimming crab	Hermit crab	Brittle star	Cut trough shell
Fe	+ 62	+266	+ 49	N.S.	+ 84
Pb	+128	+173	+ 63	N.S.	+195
Cr	+ 66	+228	+ 36	N.S.	N.S.
Hg	+ 58	+ 52	N.S.	N.S.	N.S.
Zn	N.S.	+ 23	N.S.	+ 65	N.S.
Ni	+ 51	N.S.	N.S.	N.S.	N.S.
Cu	N.S.	N.S.	N.S.	N.S.	N.S.
Cd	N.S.	N.S.	N.S.	N.S.	N.S.

(*) probability > 0.05; N.S. = not significant

Figure 2 **Total concentrations of iron (g/kg) in the <63 μm fraction (left columns) and the 63-500 μm fraction (right columns) of the eight stations**



present in the total sediment (i.e. < 500 μm). The total iron content of the 63-500 μm fraction was determined by substracting the < 63 μm value from the iron concentration in the < 500 μm fraction. The total mud fraction decreased seawards (from ca 4.2 to 0.12 g/kg) up to about 20 miles, while the coarser fraction fluctuated in a narrower range between ca 2.1 and 2.9 g/kg. This indicates that iron, as to be expected is bound primarily to the mud fraction.
Dutch investigators reported that there seemed to be no significant increase of the heavy metal content in the sediments of the titanium dioxide dumping area in the long run (Van Zwol and Bos, 1990).
In the German Bight on the other hand, higher concentrations were noted, traces of the dumping being detectable some 200 nautical miles North of the disposal area (Deutsches Hydrographisches Institut, 1985).

3.3. Biota

Results are reported in tables 3 to 7. There was neither a clear temporal trend nor evidence of accumulation of metals in benthic organisms due to the dumping of titanium dioxide waste. This was also observed in previous work (Baeteman et al., 1987).
In and around a Dutch disposal site, no significant differences in heavy metal content could be detected in hermit crab (Van Zwol and Bos, 1990). In a more critical area, the German Bight, increased heavy metal concentrations have been recorded in the epidermal tissues of dab (*Limanda limanda*). In this area however, the flushing time is much longer compared with the open North Sea (Dethlefsen et al., 1987).
Disregarding the dumping area as such there appeared to be spatial differences in concentrations among the five Northern (D1, D2, R1, R2, R3) and the three Southern stations (R4, R5, R6).
The pattern was not completely the same for all trace metals and organisms, but on the whole, the Southern area showed higher concentrations than the Northern area.
To obtain a clearer picture, the average concentrations of both areas were compared statistically (t-test). Significant differences at the 95 % level are reported in table 8. They all indicated higher concentrations in the Southern area. The opposite effect was not noted. Especially iron, lead and chromium showed a significant difference in concentrations. Copper and cadmium gave no response at all. Regarding the benthic organisms used in this investigation, sea star and swimming crab appeared to be the best indicator species for the accumulation of trace metals, brittle star being rather valueless.

Conclusions

The dumping of acid waste from the titanium dioxide production over a period of five years did not have any apparent influence on the heavy metal content of the water, sediment and benthic organisms. This confirms the previous findings (Baeteman et al., 1982, 1987) and is due to the favourable hydrodynamic pattern of the chosen dumping site. Nevertheless, large amounts of heavy metals associated with particulate matter can be carried over long distances and be deposited in areas where conditions for sedimentation are more favourable, thus contributing significantly to the heavy metal load in these areas (Carlson, 1986). For this reason, all dumpings were banned.
The trace metal concentrations reported in this paper are useful as

reference values for further ecological monitoring of Belgian coastal waters.

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Samenvatting

Zware metalen in het Belgisch lozingsgebied voor zure afvalstoffen van de titaandioxyde-industrie (1985-89)

Gedurende de onderzoeksperiode werden twee stations in het lozingsgebied en zes referentiestations bemonsterd.
In water en sediment werd alleen ijzer, een sleutelparameter, bepaald. In benthos werden Fe, Cr, Ni, Zn, Pb, Cu en Cd gedoseerd.
Het ijzergehalte (0,06-0,08 mg/l) was zeer gelijklopend in de dumpingzone en in vijf referentiestations. In het station dichtst bij de kust echter waren de concentraties twee-

tot driemaal hoger, hetgeen wijst op de invloed van inputs via waterlopen.
Een evolutie in de tijd werd niet vastgesteld. Een tekort aan opgeloste zuurstof werd niet genoteerd en markante verschillen tussen de acht zones kwamen niet voor. Dit toont aan dat de oxydatie van Fe^{++}, de voornaamste component van de afvalstroom, geen meetbare gevolgen in de waterkolom veroorzaakte. Abnormaal lage pH-waarden werden niet vastgesteld.
In de sedimenten kon geen tijdsevolutie in ijzerconcentratie worden genoteerd. Er kwamen geen hogere gehalten in het lozingsgebied voor. De ijzerconcentratie bleek niet rechtstreeks in verband te staan met het dumpen van titaandioxyde-afval maar met inputbronnen in het algemeen. De afstand van de kust speelt hierbij een belangrijke rol. Het ijzergehalte in de totale slibfractie (< 63 μm) verminderde zeewaarts toe (van ca 4,2 tot 0,12 g/kg) tot ongeveer 20 zeemijl.
In zeesterren (*Asterias rubens*), heremietkreeften (*Pagurus bernhardus*), zwemkrabben (*Macropipus holsatus*), slangsterren (*Ophiura texturata*) en strandschelpen (*Spisula substruncata*) was er noch een tijdstrend noch accumulatie van metalen te wijten aan het lozen van titaandioxyde-afval vast te stellen. Aanzienlijke hoeveelheden zware metalen aan materie in suspensie geadsorbeerd kunnen echter over grote afstanden worden verplaatst vooraleer te sedimenteren. Om deze reden werden alle lozingen vanaf 1990 verboden.

Résumé

Les teneurs en métaux lourds dans la zone belge de déversement de rejets acides de l'industrie du dioxyde de titane (1985-89)

Pendant la période d'investigations, deux stations situées dans la zone de déversement et six stations de référence furent l'objet d'un programme de surveillance.
Dans l'eau et les sédiments, seul le fer, qui est un paramètre-clé, a été dosé. Dans le benthos, d'autres métaux (Fe, Cr, Ni, Zn, Pb, Cu et Cd) ont été déterminés.
La teneur en fer (0,06-0,08 mg/l) était similaire dans la zone de déversement et dans cinq stations de référence. Dans la station située le plus près de la côte, les concentrations étaient deux à trois fois plus élevées, ce qui s'explique par les apports des cours d'eau. Une évolution dans le temps n'a pas été constatée.
Un manque d'oxygène dissous n'a pas été détecté et des différences marquantes entre les huit zones n'ont pas été notées. Ceci démontre que l'oxydation de Fe^{++}, le composé principal des rejets, n'avait pas de répercussions mesurables dans la colonne d'eau.
Des valeurs de pH anormalement basses n'ont pas été constatées.
Dans les sédiments, on n'a pas constaté d'évolution temporelle des concentrations de fer. Des teneurs plus élevées n'ont pas été mesurées dans le site de déversement.
La concentration en fer n'était pas en relation directe avec le rejet de déchets de l'industrie du titane, mais avec des sources d'apports telluriques en général. La distance par rapport à la côte joue ici un rôle important. La teneur en fer dans la fraction totale (< 63 μm) diminuait (de ± 4,2 à 0,12 g/kg) à mesure que l'on s'éloignait de la côte et ce, jusqu'à environ vingt milles marins.
Dans les étoiles de mer (*Asterias rubens*), bernards l'hermite (*Pagurus bernhardus*), étrilles (*Macropipus holsatus*), ophiures (*Ophiura texterata*) et spisules (*Spisula subtruncata*), ni une évolution temporelle, ni une accumulation de métaux due aux déversements des rejets , n'ont pu être constatées. Cependant, des quantités considérables de métaux lourds liés à la matière en suspension peuvent être entraînées sur de longues distances avant d'être déposées. Pour cette raison, tout déversement a été interdit à partir de 1990.