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EFFECTS OF TITANIUM DIOXIDE INDUSTRY WASTE DUMPING ON SEA WATER CHEMISTRY

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Abstract—An investigation was made to determine the influence of the dumping of a 1000 ton day^{-1}, on the average, of acid–iron waste from the titanium dioxide industry into the shallow but turbulent Southern Bight of the North Sea. This waste contains some 20% sulfuric acid and 2% iron. After the passage of the barge that discharges 10 ton of waste min^{-1} into its wake, the vertical and horizontal distributions of the pH, iron-concentration and turbidity were measured as a function of time. It appeared that a few seconds after the discharge and for a very brief period, the pH was down to approx. 4 and the Fe-concentration was 13 mg l^{-1}. More than 1 min after the discharge a pH below 6 and an iron-level above 3 mg l^{-1} could not be detected anywhere. The measured factor for waste dilution by sea water, based on the observed acid and iron concentration in the waste and in the discharge track, were around 5000 after 5 min, 9000 after 10 min and 80,000 after 20 min. Before and long after the dumping, the total iron-concentration in this Southern Bight area was around 100 μg l^{-1}, but this high level might be due to natural causes.

INTRODUCTION

The production process of titanium dioxide, the most commonly used white pigment, usually involves dissolving a titanium–iron ore, ilmenite, in sulfuric acid. The resulting waste by-products, called acid–iron waste, can contain up to 20% sulfuric acid and 15% ferrous sulfate as well as low quantities of other mineral pollutants. Their disposal poses serious problems. It takes place either through deep-well storage or through discharge in the sea. In Europe, direct dumping into the sea or near-shore waters is predominantly applied. The possible adverse effects of this method on the marine environmental quality are the subject of serious concern and of an intense controversy (Renzoni, 1973; Anonymous, 1974, 1976).

For the New York Bight, a thorough evaluation of the effects of acid–iron waste disposal on the physical–chemical parameters and on the summer distribution of standing crops has been carried out by Vaccaro *et al.* (1972). Weichart (1975a,b) has studied the effects of acid–waste dumping in the German Bight. A concise but complete review of other related investigations including laboratory experiments of the acid–iron waste toxicity to plankton, benthos and fishes has been published by Rachor & Dethlefsen (1976). In general, it appeared that major harmful effects can be avoided if dilution after discharge is high, if no accumulation takes place in the discharge area and if other ecological factors are favourable. More recently, the view of these authors on the biotoxicity of acid–iron waste has changed considerably since in the German Bight they observed an increased epidermal papilloma incidence in *Limanda limanda* (Dethlefsen & Watermann, 1980).

Hitherto, no data were available on the effects on the sea water chemistry of the daily dumping of 1000 tons of acid–iron waste, on the average, in the Southern Bight of the North Sea, 15 km off the Belgian coast (see Fig. 1a). The 69 m long barge circles at 17 km h^{-1} around the site 3° 00′E–51°30′N (site A in Fig. 1b) with a 1.5 km diameter and discharges 1000 ton of liquid and solid waste, in a ratio of about 20 to 1, in its wake through several tubes situated right behind the propeller. The dumping area is characterized by a depth of only approx. 23 m, a relatively strong current, at 3 cm s^{-1}, from the English channel to the N-NE, parallel to the Flemish coast, and prevailing winds from the W-SW. De Clerk & Van de Velde (1974) found a normal fish fauna off the Belgian coast and had no indication of dead, affected or damaged fishes in the dumping area.

The present work was aimed at evaluating the effect of the acid–iron waste dumping in this area on the pH, iron content and turbidity of the sea water and their distribution as a function of time and space. Other aspects of the same research project dealt with the mechanisms and kinetics of the ferrous iron oxidation and precipitation (Van Grieken *et al.*, 1980) and with the adsorption of heavy metals on the resulting ferric hydroxide (Chakravorty & Van Grieken, 1982).

EXPERIMENTAL METHODS

Analysis procedures

The waste samples were analysed as follows. The acid content was determined by a potentiometric titration with 1 N NaOH. Ferrous iron was determined by spectrophotometry (APHA, 1971) with orthophenanthroline at 510 nm, after a suitable dilution step, using a Cecil Instruments 51/0752 spectrophotometer. Total iron was determined similarly, after reduction with hydroxylamine. Aluminium was assessed at 535 nm with eriochrome-cyamine. Sodium and magnesium were determined by atomic emission spec-

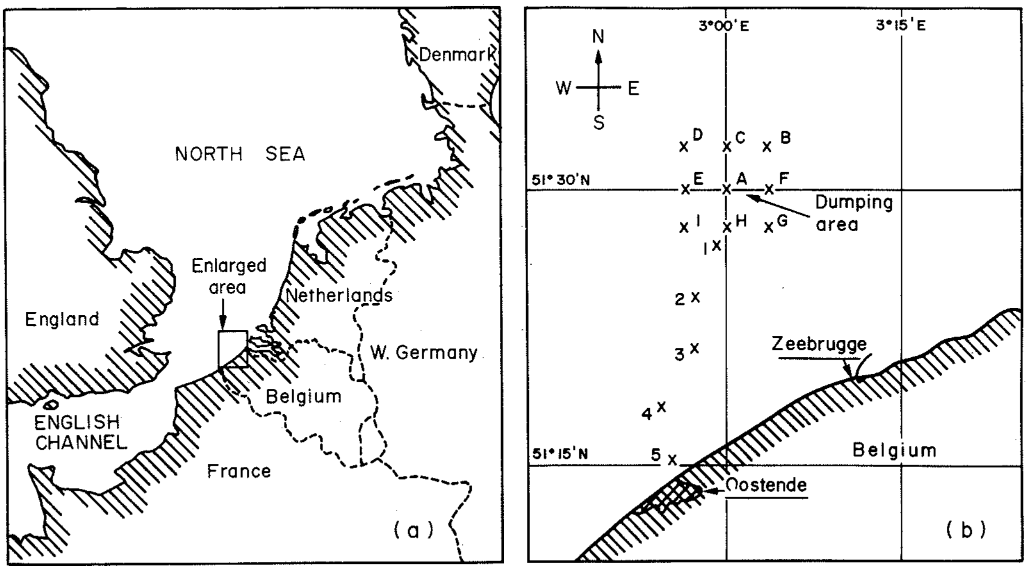

Fig. 1. (a) Map of the North Sea, with the dumping area indicated; (b) detail, with the sampling stations and the theoretical dumping site A.

trometry, and cadmium by atomic absorption spectrometry, both using a Perkin–Elmer 103 unit with air–acetylene flame. The energy-dispersive X-ray fluorescence analysis was based on a procedure developed by Van Dyck & Van Grieken (1980). It included neutralization of the waste with NaOH, filtering off and analysing the ferric hydroxide precipitate and evaporating some of the eluate and analysing the residue.

The *in-situ* profiles of pH, temperature, salinity and dissolved oxygen content were measured by lowering a probe from the research vessel. Another probe was used to map the turbidity profiles; the calibration was done with aqueous formazine suspensions (1 turbidity unit corresponds to 1 $\mathrm{mg\,l^{-1}}$ formazine). To measure the profiles near the surface horizontally, perpendicularly to the wake of the barge, sea water from -2 m was continuously pumped up aboard the research vessel into a buffer barrel in which the probe was immersed. For the determination of iron in the sea water, discrete 5 l. samples were taken at different depths with a Nansen bottle and aliquots were analysed for iron by colorimetry with bathophenanthroline (APHA, 1971) that is more sensitive and selective for iron than orthophenanthroline (Koenings, 1976).

Table 1. Average composition of the acid–iron waste

Parameter	Measured concentrations In the liquid phase* (g/100 ml)	 In the solid phase (g/100 g)
H_2SO_4	20.5	—
Total Fe	1.4	3.0
Fe(II)	1.35	—
Na	0.05	—
Mg	0.50	0.40
Al	0.25	5.7
Si	—	8.0
K	0.03	0.30
Ca	0.07	2.1
Ti	0.25	14
V	0.04	0.02
Cr	0.15	0.07
Mn	0.09	0.33
Sr	<0.005	0.06
Ba	0.01	0.15
Sc, Co, Ni, Zn, Ga, Ge, As, Se, Br, Rb, Y, Cd, Ce, Nd, Hf, Th, U	<0.02	<0.04

*Specific density of the liquid phase = 1.21 g $\mathrm{cm^{-3}}$, *m*-acidity = 4.3 $\mathrm{eq\,l^{-1}}$, *p*-acidity = 4.9 $\mathrm{eq\,l^{-1}}$, OH-acidity = 5.3 $\mathrm{eq\,l^{-1}}$.

Field measurements and sampling

Five campaigns were carried out using the research vessel "MSI". Four took place around the time of a dumping event, namely 13 July, 25 September and 27 November, 1979 and 26 February, 1980. One took place 24 h after a dumping on 29 November, 1979.

To map the vertical profiles, a buoy was dropped into the water in the middle of the dumping track and the research vessel stayed near the buoy. To assess perpendicular surface profiles, the research vessel crossed the track several times perpendicularly to the moving direction of the dumping barge. Several times the research vessel followed behind the barge at a certain distance, or approached it in its wake.

RESULTS

Composition of the acid–iron waste

Four waste samples originating from the two plants in Flanders that discharge acid–iron waste into the North Sea were analysed for many parameters. The material includes both a liquid acid fraction and a sludge fraction that contains 20–50% solids on a dry weight basis. Table 1 represents the analysis results both for solid parts retained on a 0.4 μm pore-size filter and for the combination of the eluate of this sludge and the major, originally liquid, fraction of the waste. Since no significant differences were noted between the wastes from the two firms, the results were pooled. The results corresponded very well with the producers' analysis reports. Apart from Cr, no toxic elements are present in significant concentrations. The acid–iron wastes that are dumped in the

Table 2. Situation in the dumping area before the dumping events

Cruise date	Depth (m)	pH	T (°C)	Total Fe (μg l^{-1})	Wind speed (Beaufort)
13 July, 1979	2	7.97	17	<80	3–4
25 September, 1979	2	8.03	16	235	2
	5	8.01	—	245	—
	10	8.06	—	150	—
27 November, 1979	3	7.98	9.5–11.2	175	2
	6	7.97	—	120	—
	9	7.96	—	120	—
26 February, 1980	10	7.94	6.9–8.3	75	1–2
Discrete-samples	20	8.10	—	35	—
				Turbidity (ppm)	Salinity (‰)
Continuous profile	0–2	7.92	5.2	0–3	32.33
	2–6	7.92	5.2	3–6	32.33
	7	8.00	5.5	3	32.27
	8	8.02	5.7	0	32.64
	9	8.03	5.9	0	33.12
	10	8.03	6.1	0	33.20
	11–15	8.03	6.1	0	33.30

German Bight and New York Bight contain approx. 10% H_2SO_4, 5% Fe, 0.4% Ti and 0.001% Cr (Vaccaro *et al.*, 1972; Weichart 1975a; Rachor & Dethlefsen 1976), hence considerably more Fe but less acid and Cr.

Profiles of pH, turbidity and iron before acid–iron dumping

Prior to each dumping event, samples were taken in the dumping area and analysed to serve as references. The results are shown in Table 2. The iron concentration shows a great variability. The last campaign, which took place in a period of very calm weather, yielded the lowest Fe-values and the vertical profile showed a clear stratification, with a strong variation of the measured parameters between 6 and 9 m.

Vertical distribution of pH, turbidity and iron after acid–iron waste dumping

Vertical pH-profiles measured in the wake of the barge, are represented in Fig. 2 for the cruise of 26 February, 1980. It seems that the acid spot has a limited height and that it splits in two parts, perhaps one associated with the liquid waste and the other with the solid waste. A full neutralization takes places after less than 1 h. Afterwards, the pH seems to be approx. 0.10 units higher than before the dumping; if, with the pH-sensor used, this difference is significant at all, it could probably be linked to CO_2 escaping during the high acidity phase. The continuous profiles and discrete pH-measurements during the other cruises also indicated that initially the pH drops locally to 6–6.6 at the depth of 0–4 m. Lower values than pH 6 have not been noted in any case at 1 min or more after the passage of the discharging barge.

Figure 3 shows the simultaneously mapped vertical turbidity profiles. The turbidity appears to increase to 5–10 units a few minutes after the dumping. The original layer of 6 turbidity units at 5–7 m depth is disturbed by the passage of the barge, and in general, a quite persistent turbidity increase is observed at larger depth. In the cruise of 25 September, 1979, a maximum turbidity of 21 units was observed at a depth of 3–4 m after some 1–2 min.

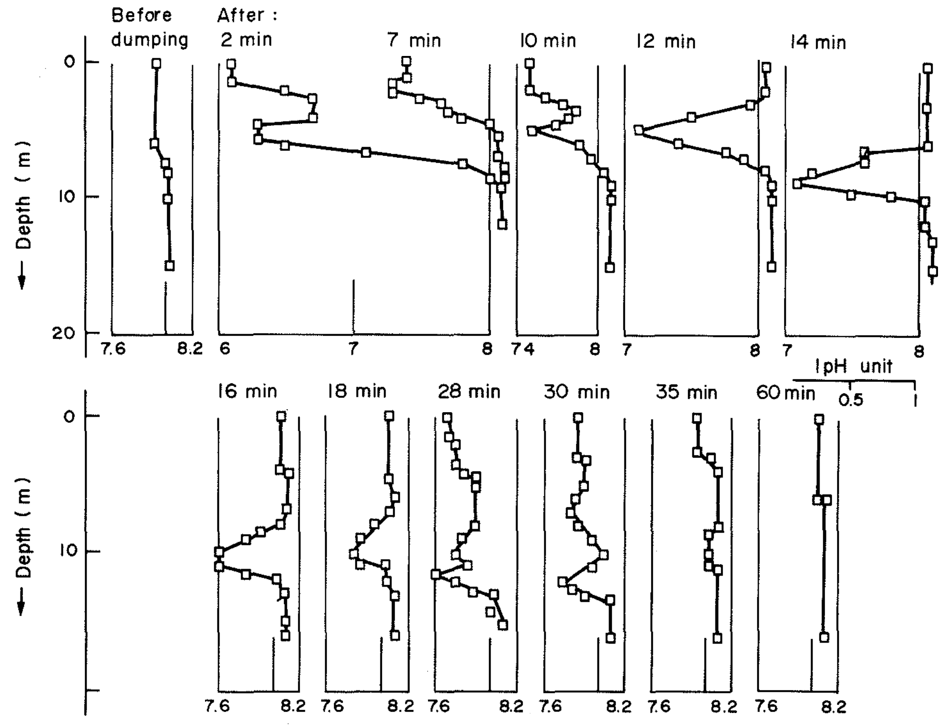

Fig. 2. Vertical pH-distribution as a function of time after the dumping.

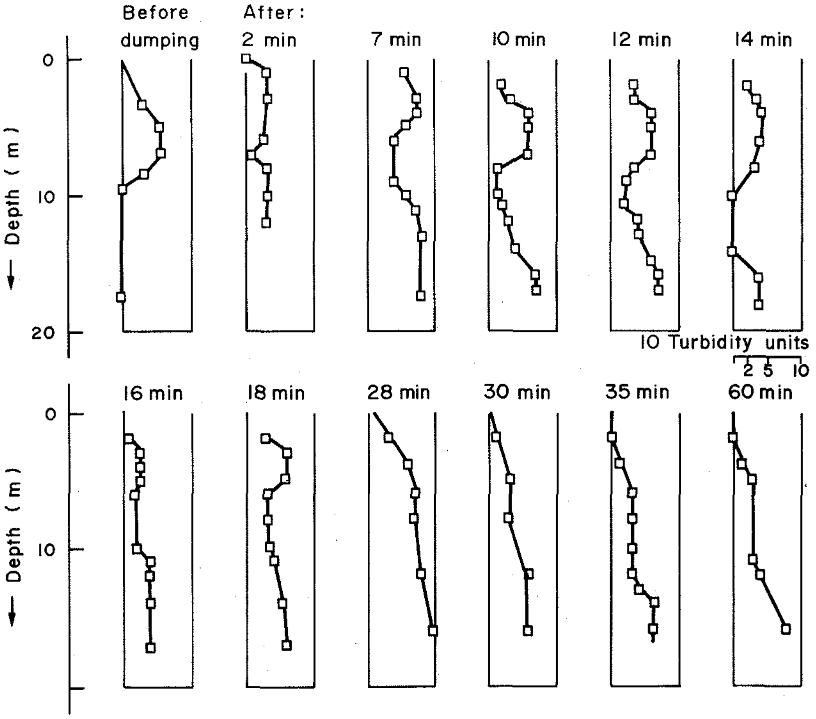

Fig. 3. Vertical turbidity-distribution as a function of time after the dumping.

Figure 4 displays the results for the total iron content of the sea water. While in one case a value of 13,400 $\mu g\,Fe\,l^{-1}$ was found near the surface at 10 s after the passage of the barge, the iron appears to be diluted down in 40 min to the 100 $\mu g\,l^{-1}$ level, which was generally found before the dumping started (see Table 2). The Fe(II) content was measured specifically by immediately adding the bathophenantroline reagent in the field: 80–100% of the total iron was found to be in the reduced and dissolved state, until, after some 15–20 min, the pH had risen to approx. 7.7.

Horizontal distribution of pH, turbidity and iron after acid-iron waste dumping

When the research vessel kept on crossing perpendicularly through the discharge track it appeared again, both from the continuous probing and the discrete sample analyses, that at 30–60 s after the barge

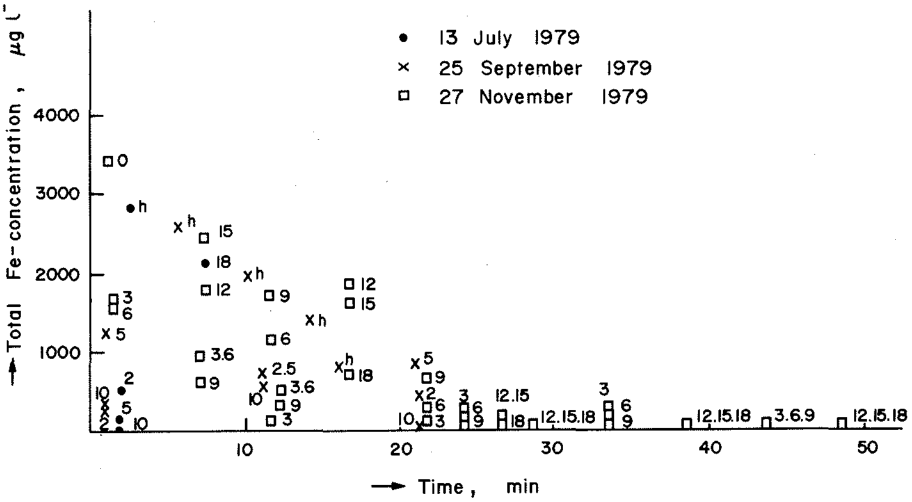

Fig. 4. Total Fe-concentrations measured as a function of time after the dumping. h = concentrations found in the track of the discharging barge during the horizontal distribution mappings at 2 m depth; 0, 2, 5, 6... = concentrations found during the vertical distribution mappings namely at depths of 0, 2, 5, 6... m. In addition, one value of 13400 $\mu g\,Fe\,l^{-1}$ was found at 2 m depth at 10 s after the discharge.

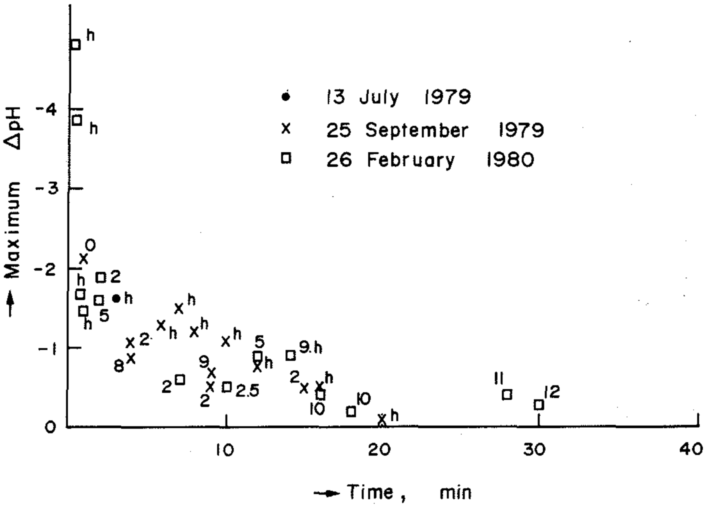

Fig. 5. Maximum pH-depressions as a function of time after the dumping. h = maximum pH-depressions found in the center of the track at 2 m depth; 0, 2, 5, 8... = maximum pH-depression found during the vertical distribution mappings, namely at depths of 0, 2, 5, 8... m.

passage, the pH was down to 6–6.5 at 2 m depth in the middle of the track, while the Fe-level increased locally to nearly 4000 $\mu g\,l^{-1}$. Normalization at 2 m depth was almost complete after some 20 min. It also appeared that the dumping track is rather narrow. Indeed, if one defines the width as the distance between the sites with half of the maximum pH or Fe-concentration change, the track is 10–20 m wide immediately after the dumping and has spread to 100 m some 10–12 min afterwards.

To check the maximum acid and iron concentration increases more accurately the research vessel also followed the discharging barge being steered as well as possible right in the middle of the wake. In three of the cruises the pH-values were assessed continuously by an *in-situ* probe, and determined on the sea water pumped up continuously aboard the research vessel and on discrete water samples collected in Nansen bottles. The time elapsed since the discharge was estimated from buoys dropped from the discharge barge. These results for a depth of 2 m in the centre of the track are included in Fig. 5. In one case, a pH of 3.1–3.8 was noted after 10 s just 20 m behind the barge; the accompanying total Fe-content was as high as 13 $mg\,l^{-1}$. Some 20 s after the release, the pH had risen to 4–5.5 and to 6.4 after 1 min. In other cases the short-time effects seemed somewhat less drastic. The reduction with time of the excess iron paralleled the reduction of the pH-depression at this depth.

Situation 1 day after a dumping

On 29 November, 1979, a campaign was held at 24 h after a dumping, to see if there was any measurable chemical pollution left. A continuous horizontal profile of pH, turbidity, dissolved oxygen and temperature was recorded at 2 m depth from the coast to the theoretical dumping site and an area of 600 km^2 around the dumping site was examined. At the different stations indicated in Fig. 1(b) samples were taken to determine the iron concentration.

Table 3. Situation between the coast and the dumping area

Station (see Fig. 1b) and local depth	27 November, 1979, approx 3 h after dumping (depth = 5 m)			29 November, 1979, approx 24 h after dumping (depth = 5 m)		29 November, 1979, approx 30 h after dumping (depth = 2 m)	
	Total Fe ($\mu g\,l^{-1}$)	pH	T (°C)	Total Fe ($\mu g\,l^{-1}$)	pH	Total Fe ($\mu g\,l^{-1}$)	pH
No. 1 (15 m)	175*	7.88	9.8	155*	7.92	160*	7.91
	130*			90*		60*	
No. 2 (10 m)	175	7.90	10.2	150	7.98	175	7.92
	110			85		80	
No. 3 (11 m)	375	7.89	9.9	370	7.90	280	7.90
	240			275		135	
No. 4 (7 m)	665	7.91	9.8	375	7.96	280	7.90
	430			245		150	
No. 5 (5 m)	670	7.91	9.0	485	7.85	530	7.78
	420			335		250	

*The upper line gives the iron concentration found after acidification, the lower line the one without acidification.

Table 4. Situation in the dumping area 24 h after a dumping event

Station (see Fig. 1b)	Depth (m)	T (°C)	Turbidity (ppm)	Dissolved oxygen (ppm)	pH	Total Fe ($\mu g\,l^{-1}$) Without acidification	Total Fe ($\mu g\,l^{-1}$) After acidification
A*	2	8.7	23	9.0	7.91	85	205
	5				7.90	235	430
	15				7.97		
B	2	8.7	18	9.0	7.90		
	5				7.95	80	175
	15				7.99	110	185
C	2	8.9	17	9.0	7.91		
	5				8.03	65	135
	15				8.04	80	180
D	2	9.0	17	9.0	7.93		
	5				7.90	45	110
	15				7.86	80	120
E	2	9.5	17	8.9	7.96		
	5				7.93	30	85
	15				7.90	40	95
F	2	9.0	23	9.0	7.93		
	5				7.90	40	160
	15				7.87	260	530
G	2	8.9	23	9.0	7.93		
	5				7.90	40	150
	15				7.90	195	380
H	2	9.7	21	8.9	7.96		
	5				7.93	120	185
	15				7.93	415	720
I	2	8.7	21	9.1	7.91		
	5				7.92	155	170
	15†				7.91	105	230

*For Sta. A the average value of three-fold measurements is given.

For the track between the coast and the dumping area, Table 3 gives the results of the iron concentration together with the results of the samples taken at the same stations on 27 November, 1979, about 3 h after a dumping. These concentrations were determined with and without acidification which gave a measure of reactive, respectively non-reactive, iron (Koenings 1976). Obviously, there is an enrichment of iron in the direction of the coast by a factor 3–4. The soluble iron concentration was always below 35 $\mu g\,l^{-1}$. The continuous profiles on this route appeared to be rather regular except near the coast and at about 3 km from the dumping place where a strong temperature and salinity increase together with a decrease of the oxygen content occurred. This effect might be due to a limited and natural local current.

In the dumping area, Stas A–I of Fig. 1(b) were monitored 24 h after the dumping. The results are displayed in Table 4. Mutual comparison of Stas C–F, D–G and E–H indicates an increase of the iron concentration in the South-East direction, which is most noticeable in the samples taken at a depth of 15 m. In agreement with the extremes found in the continuous profiles from the coast to the dumping site, we found temperature and oxygen extremes in Stas E and H. Relative to the data of 27 November, 1979, taken before dumping (given in Table 2) no significant differences in pH, Fe-content and temperature could be observed within this area.

DISCUSSION

The above results indicate that, in the wake of the discharge barge, the acid and iron concentrations are increased over a width of 10–20 m just after the dumping, and of 100 m some 10 min later. The acid mass sinks slowly, on the average at a rate of about 0.5 m min^{-1}, and it seems to split up into two fractions of which the heavier one probably contains the solid sludge.

The maximum pH depression is 4 units a few seconds after the discharge, but it is swiftly reduced to 2 units some 1 min later, and no effect can be detected near the surface at 20 min after the dumping and at 40 min for the deeper layers. The very important buffer capacity of sea water but also the appropriate dumping technique by which the waste is discharged into the turbulent wake water behind the barge, and the strong wave and current action in the North Sea, all contribute to an efficient neutralization of the acid iron waste. The total iron concentration seems to undergo a similar dilution effect as the acid. The waste dilution as a function of time can probably be expressed most quantitatively via a factor of dilution with sea water. To estimate to which waste dilution factors the measured pH-changes correspond, two aliquots of 200 μl of ten-fold diluted acid–iron waste were carefully titrated with North Sea water and the pH was monitored with a glass electrode. Also, the expected pH-depressions were calculated from the acid-iron waste composition (see Table 1) using formulae given by Van Grieken *et al.* (1980). Both the experimental and theoretical results are represented in Fig. 6. From this curve and from the data in Fig. 5, one can calculate the average acid–iron waste dilution factors as a function of time for the cruises of 13 July, 1979, 25 September, 1979 and 26 February, 1980. These factors are included in Table 5, second column.

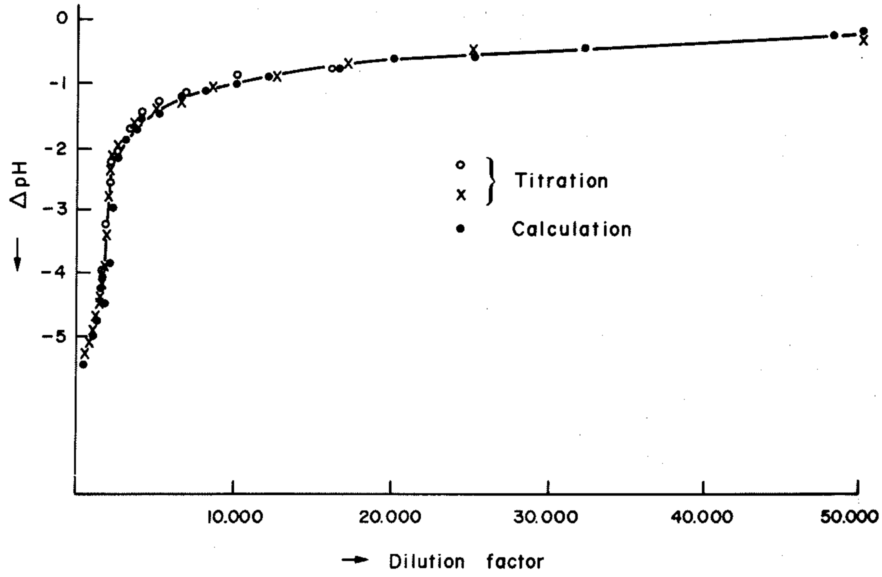

Fig. 6. Influence of the acid–iron waste on the pH of sea water as a function of its dilution.

Also from the average iron content of the waste, as listed in Table 1, and from the average iron concentration measured in the wake water, such factors can be derived. They are also given in Table 5, third column and agree reasonably with the former set. Relative to the values reported by Weichart (1977), the present dilution factors are much larger. This discrepancy is due to differences in discharge characteristics and in dilution behind the propeller of the ship and/or it is due to the different currents and wave pattern in the Southern Bight of the North Sea.

Applying the IMCO-formula for calculating the dilution capacity in a ship's wake (Intergovernmental Maritime Consultative Organization, 1975) yields a predicted dilution factor of 3100 after 5 min, somewhat below the present value given in Table 5. It should be borne in mind, however, that the combination of parameters for ship speed and length do not fully correspond with the range in which the formula is directly applicable and that the formula is strictly intended for pure liquid substances only. The IMCO-formula predicts an increase of the dilution factor with the time t by $t^{0.4}$. The dilution factor variation up to 10 min after the dumping, as calculated from the measured Fe-concentrations (Table 5, column 3) corresponds perfectly with this law, within 10%, while for the pH-based diluted factor (Table 5, column 2) the discrepancies are limited to 30% for all data points.

Table 5. Dilution of the waste with sea water as a function of time

Time since discharge	Dilution factor		
	Based on pH (using Fig. 6 and average measured pH-values)	Based on Fe-conc. (using Table 1 data and average measured Fe-concentration)	Values reported by Weichart (1977)
10 s	1100	1200	
1 min	2000	2800	
2 min	2500	4400	
3 min	3500	5200	
4 min	4200	5700	
5 min	4800	6100	
6 min	5200	6500	
7 min			1000
8 min	7000	7400	
10 min	8500	8500	
15 min	20,000	15,500	
20 min	> 50,000	85,000	5000
70 min			10,000
200 min			50,000
700 min			100,000

The turbidity change of the sea water was never found to be very pronounced, relative to the already high natural turbidity of the Southern Bright water that is undoubtedly linked with the shallow depth, sandy bottom and strong turbulence. The local turbidity increase due to the acid–iron waste is, of course, also related to the extent and kinetics of the ferrous ion oxidation and precipitation in sea water. These processes will soon be discussed elsewhere (Roekens & Van Grieken, 1983a,b).

The total Fe-concentrations that were found before and 1 day after the dumping, are around 100 $\mu g\, l^{-1}$, hence relatively high. Indeed, the theoretical solubility of Fe(III) in sea water is 0.5–5 $\mu g\, l^{-1}$ (Roekens & Van Grieken, 1983a,b). Riley & Skirrow (1973) and Horne (1969) indicate 2 and 10 $\mu g\, l^{-1}$, respectively, as a mean value of the iron concentrations in the ocean. Vaccaro *et al.* (1972) measured a maximum concentration of 832 $\mu g\, l^{-1}$ in a New York Bight area where large amounts of brown flocculent material were visible.

In conclusion, it can be stated that, except for the surface water in the very first seconds after the discharge, the pH of the sea water can nowhere be found to be below 6 and the iron concentrations are nowhere above 3 mg l^{-1}. Some 40 min after the passage of the barge, the pH, iron concentration and turbidity are not detectably different from their long-term values in the dumping area or from their values in the neighbouring area. As to these parameters, the effect of acid–iron waste dumping into the shallow but turbulent Southern Bight is certainly not very pronounced with the applied technique of discharging some 10 tons of waste min^{-1} in the wake water of the barge moving at 17 km h^{-1}. Whether the long term practice of this dumping has any adverse effect or results in a significant accumulation of harmful waste products in other parts of the North Sea remains to be investigated.

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