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A review of the effects on aquatic ecosystems of acid iron waste from the production of titanium dioxide by the sulphate process.

Norwegian Institute for Water Research NIVA

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Abstract:

Damaging effects of acid iron waste to biota have been demonstrated in the vicinity of coastal and estuarine outfalls. The toxic properties have been confirmed in laboratory studies with algae, invertebrates and fish. So far it appears that the toxicity is associated with either decreased pH (below pH 6.0-7.0) and/or iron concentrations above at least 0.5-1 mg Fe/l. However, due to the complex nature of the waste and its fate in the aquatic environment causal relations are difficult to assess. Leakage of metals from precipitated iron hydroxide flocs may be among the serious stress factors. In dumping areas of the open sea there are few and uncertain observations of harm to biological communities. With the possible exception of two estuarine recipient areas the risk of accumulation of waste constituents appears to be small.

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A REVIEW OF THE EFFECTS ON AQUATIC ECOSYSTEMS OF ACID IRON WASTE FROM THE PRODUCTION OF TITANIUM DIOXIDE BY THE SULPHATE PROCESS

20 January 1983

Project leader : Jon Knutzen

For the administration: J.E. Samdal

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PREFACE

The present report has been sponsored by Kronos Titan A/S, Fredrikstad, Norway. Thanks are due to Erik Lund for giving me access to reports of the American consultants firm Energy Resources Co. Inc. (ERCO) and for other information about the production of titanium dioxide and the sulphate process.

My thanks also go to Dr. Herman Michaelis of the Forschungstelle Norderney, FRG, for information about work at this institute and for calling my attention to studies in the river Weser; further to Karl-Johan Lehtinen of the Swedish Water and Air Pollution Research Institute, for information about Finnish publications and for a preprint of his own work.

Finally, I am grateful to my colleagues Pirkko Rygg for translation of papers in Finnish, without which the report would have been even more of a torso; and to Norman Green for looking over that part of the English which now is acceptable.

Oslo, 20 January 1983

Jon Knutzen

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1. INTRODUCTION

The dumping of acid iron waste from the titanium dioxide production by means of the sulphate process has been the cause of long-standing scientific investigations, and of evaluation and negotiations within international organizations such as the Oslo and Paris Commissions and the Commission of the European Communities.

Recent actions by the international environmental protection organization Greenpeace against dumping in the New York Bight and the North Sea have brought the question into public focus. The viewpoint and arguments of Greenpeace have been summarized by Pickaver (1982).

It has been the aim of this review to update a previous synopsis (Knutzen 1972) and to present in a relatively concise way the facts known about waste effects on freshwater and marine organisms and communities.

Unfortunately, some of the work has not been published. Further, much valuable information is only accessible in journals with mainly national circulation, in the form of reports brought forward as part of the activities within international organizations, as consultant's work for the industry or as internal reports of national water management bodies. Some of the latter two types of presentation have not been available for the present review. This difficulty has in part been overcome by citing from other papers referring the inaccessible results.

2. PRODUCTION, USE AND RAW MATERIALS

In 1972 estimated world production of titanium dioxide was 2.5 mill. tons per year (Anonymous (SACSA*) 1976), and it has not changed much in the last decade (E. Lund, pers. comm.). The product is a white pigment used in paint and lacquer, paper, plastics, rubber, floor covering, ceramics, and for various other purposes, such as ingredients of cosmetics and pharmaceuticals.

In order of increasing TiO_2-content the chief raw materials are:

- Norwegian and Australian ilmenite (respectively about 45 % and 55 % TiO_2)
- Canadian slag (a by-product from iron production, about 70 % TiO)
- Enriched ores (max. 89 % TiO_2)
- Synthetic rutile
- Rutile (~ 95 % TiO_2)

For the extraction of titanium it is mainly used chlorine under high temperature or digestion with sulphuric acid. With the exception of the Du Pont process, the less waste producing chloride process has mostly been used with rutile raw material. It is the ilmenites, however, which represent the large reserves of titanium containing ores. Another decisive factor in the choice of technology has been the comparative cheapness of the sulphate process. Only the sulphate process will be considered further here.

Of the total production capacity of 1.0 mill. tons per year in Western Europe the sulphate process represents more than 85 % (E. Lund, pers. comm.). According to Lassus and Maggi (1977) the sulphate process stands for above 70 % of the total world production.

* Standing Advisory Committee for Scientific Advice, Oslo and Paris Commissions

3. SULPHATE PROCESS

Schematically, the process can be described in terms of the following stages (Anonymous 1976, SACSA of the Oslo and Paris Commissions):

1) Digestion

$H_2SO_4 + TiO_2 \rightarrow TiOSO_4 + H_2O$

First waste stream: Non solubles (SiO_2, TiO_2, other metal oxides).

2) Reduction of dissolved trivalent iron (addition of Fe)

$Fe + Fe^{3+} \rightarrow Fe^{++}$

3) Precipitation of ferrous sulphate

This takes place after cooling and evaporation in vacuum. The precipitate $FeSO_4 \cdot 7H_2O$ is a green slurry called copperas and constitutes one of the main wastes (second waste stream).

4) Hydrolysis and washing

$TiOSO_4 + H_2O \rightarrow TiO_2\ (H_2O)_2 + H_2SO_4$

After filtration of the titanium compound the filtrate is about 20 % sulphuric acid with impurities (third waste stream). Washing of the hydrated titanium dioxide gives about 10 % sulphuric acid as the fourth waste stream.

5) Calcination

This takes place at about 900 °C and transforms the amorphous hydrate to crystalline form.

Note: Steps 2 and 3 are not necessary when the production is based on slag or enriched ilmenite ore.

4. WASTE

Both quantities and actual composition of the acid ferrous iron waste per produced unit of titanium white are rather variable, depending on site specific factors. The theoretically largest quantities of waste come from processing low grade ilmenite ore. The TiO_2-working group under SACSA of the Paris and Oslo Commissions (Anonymous 1976) states that waste production from Norwegian ilmenite, measured in 100 % H_2SO_4 and $FeSO_4$, is ca. 2.3 tons and 2.1 tons, respectively. (The latter figure corresponds to 3.85 tons $FeSO_4 \cdot 7H_2O$). Adding other metals in solution and insolubles gives close to 5 tons of concentrated waste per ton titanium dioxide.

In a later report from SACSA (Anonymous 1982a) it is stated that each ton of TiO_2 produced from ilmenite results in 5.6 tons of diluted H_2SO_4 waste (concentration not stated). Comparatively, the use of slag should result in 7.9 tons diluted sulphuric acid. However, measured in concentrated acid, the sulphuric acid waste may be lower from the slag based process (E. Lund, pers. comm.). In the same report the figure 4 tons per ton TiO_2 is given for the formation of copperas ($FeSO_4 \cdot 7H_2O$).

In practice, quantitites and concentrations depend much upon factors such as composition of raw materials, impurities in the sulphuric acid, degree of acid recycling or utilization of the iron waste, possible use of neutralization, in factory dilution or partioning of waste for different ways of disposal.

Examples of waste composition from different sources are given in Table 1. Consideration of the variation in composition is important in regard to recipient and biotest studies, in particular when comparing results from tests conducted with different waste waters. Information which is required to assess the reliability of the analysis data are not available.

Table 1. Approximate composition of waste dumped or discharged from different sources.
Concentrations in mg/l when not otherwise stated.

Components \ Source	Titan-gesellschaft Leverkusen [1]) (Germany)	Titan-gesellschaft Leverkusen [2]) (Germany)	Titan-gesellschaft Nordenham [3]) (Germany)	N.L. Industries Sayreville [4]) (USA)	Can. Tit. Pigments Varennes [5]) (Canada)	Tioxide Canada Tracy [5]) (Canada)	Vuorikemie Oy [6]) (Finland)	British Titan Prod. [7]) (England)	Kronos Titan A/S [8]) Fredrikstad (Norway)	La Montedison, Scarlino [9]) (Italy)	Thann & Mulhouse Le Havre [9]) France)	Tioxide S.A., Calais [9]) (France)	Bayer S.A., Anvers [10]) (Belgium)	Du Pont Delaware [11]) (USA)
ph					1.1-1.5	1.0-1.5	1.0	1.0	1.5	0.2	0.6	0.4		
Acidity (mg $CaCO_3$/l)					$4.9-6.6 \cdot 10^3$	$13-19 \cdot 10^3$								
COD					55-90	150-370								
H_2SO_4	$170 \cdot 10^3$	$135 \cdot 10^3$	$125 \cdot 10^3$	$< 130 \cdot 10^3$			$24 \cdot 10^3$	$20 \cdot 10^3$	$6.1 \cdot 10^3$	$110 \cdot 10^3$	$33 \cdot 10^3$	$57 \cdot 10^3$	$< 250 \cdot 10^3$	$48 \cdot 10^3$
Sulphate					$5-20 \cdot 10^3$	$12-32 \cdot 10^3$	$45 \cdot 10^3$							
$FeSO_4$	$280 \cdot 10^3$	$230 \cdot 10^3$	$175 \cdot 10^3$				$32 \cdot 10^3$		$7.7 \cdot 10^3$					
As Fe	$100 \cdot 10^3$	$85 \cdot 10^3$	$65 \cdot 10^3$	$33(53?) 10^3$	$0.4-0.7 \cdot 10^3$	$0.7-1.3 \cdot 10^3$	$12 \cdot 10^3$	$8 \cdot 10^3$	$3 \cdot 10^3$	$48 \cdot 10^3$	$8 \cdot 10^3$	$4.9 \cdot 10^3$	$< 20 \cdot 10^3$	
$MgSO_4$	$26 \cdot 10^3$	$23 \cdot 10^3$	$12.5 \cdot 10^3$						10^3					
As Mg	$5.2 \cdot 10^3$	$4.6 \cdot 10^3$	$2.5 \cdot 10^3$						$3.2 \cdot 10^3$				$9 \cdot 10^3$	
$TiOSO_4$	$11.2 \cdot 10^3$	$16 \cdot 10^3$	$18 \cdot 10^3$											
As Ti	$3.4 \cdot 10^3$	$4.8 \cdot 10^3$	$5.5 \cdot 10^3$		35-130	140-230	$1.3 \cdot 10^3$		160	$2.6 \cdot 10^3$	550		$2 \cdot 10^3$	$1.5 \cdot 10^3$
Diss. Ti					30-110	70-130	$1.1 \cdot 10^3$							
$MnSO_4$	$1.6 \cdot 10^3$	10^3	900											
As Mn	580	350	310				190		19	585	300	67	300	$1.3 \cdot 10^3$
$VOSO_4$	$1.2 \cdot 10^3$	600	560											
As V	500	190	180		12-60	45-50	40		12	275	19	190	300	165
$Cr_2(SO_4)_3$	90	180	175											
As Cr	23	46	45	5	5	10-20	7		4	40	7.5	57	200	88
Zn				25	0.3	20-60	75		1	19	103	11		40
Pb				5	0.3	< 0.5	0.4		< 0.1	10	1.2	0.5		12
Co				7					1			2.2		11
Ni				4	< 0.2	< 0.1-2.5	5		0.7			2.2		11
Cu				0.5	< 0.1	< 0.2	1		< 0.1	0.4	2.3	0.1		5.3
Cd					$< 2 \cdot 10^{-2}$	< 0.1	$< 2 \cdot 10^{-2}$		$< 5 \cdot 10^{-2}$	0.6	3.4	0.1		3.8
Hg					$< 10^{-3}$	$< 5 \cdot 10^{-3}$	10^{-3}			$4 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$< 4 \cdot 10^{-3}$		
Al							70			385		$1.4 \cdot 10^3$	$< 10^4$	810

[1,2]) Recalculated after Kinne and Schumann (1968) and Kayser (1969), respectively, on the basis of information about relative proportion of acid and copperas in waste and assuming specific weight 1.25 (Weichart 1972). Probably the test waste of both Kinne and Schumann and Kayser had a slightly higher specific gravity than 1.25. According to addendum in Kayser (1968) the normality of H_2SO_4 was 4 and of $FeSO_4$ 4.2, which means that the concentration of $FeSO_4$ and iron was above 300 mg/l and 100 mg/l, respectively.

[3]) Calculated after Weichart (1975a), assuming a specific gravity of 1.25 (Weichart 1972) and percentages on weight basis. The quoted figures concern waste dumped in the German Bight. Residual acid is discharged into the Weser estuary (Wienecke 1962).

[4]) Acidity concentrations from Ketchum and Ford (1948), Owen (1956) and Peschiera and Freiherr (1968), otherwise from Vaccaro et al. (1972). Two different values are given for iron concentration. Probably ~ $33 \cdot 10^3$ mg/l is correct, as this concentration also is stated in a later laboratory study (Grice et al., 1973). Dumped in New York Bight until 1982.

[5]) From ERCO and ECO-RESEARCH (1980). Metal levels quoted are total concentrations, with regard to iron the dissolved species constituted more than 90 % of the total. Both effluents are discharged to the St. Lawrence River.

[6]) From Häkkilä (1978). (Lead, nickel and copper concentrations from Häkkilä et al. 1978.) Discharged to the Bothnian Bay.

[7]) From Wilson and White (1974). Discharged to the Humber estuary.

[8]) From Knutzen et al. (1974) and Bokn et al. (1976). Diluted with river water before discharge. Discharge of ferrous sulphate (copperas) reduced with 1/3 in later years.

[9]) From Lassus and Maggi (1977). The effluents are respectively dumped in the Tyrrhenian Sea, discharged to the river Seine and discharged to the English Channel. For zinc, copper, cadmium and mercury the concentrations concern waste used in test. The iron concentrations of waste used in tests were 44 g/l (Montedison), 12.5 g/l (Thann et Mulhouse) and 4.7 g/l (Tioxide).

[10]) From de Clerck and van de Velde (1974). Dumped in the North Sea.

[11]) Calculated from Pesch et al. (1974). Discharged 65 km southeast of Delaware Bay.

There is no readily available survey showing total waste from the world's titanium dioxide industry. However, a report to the Commission of the European Communities (1978) lists production units, processes and capacities. (It should be warned that the title of this report is a unique misnomer, as its treatment of "environmental impact" is limited to a dozen paper clippings of dubious informative value.)

Not even in Europe has it been possible to give complete accounts of wastes and disposal methods, in spite of the Oslo and Paris Conventions. In a report from The Secretariat of the Paris Commission (Anon. 1982b, originally from 1980) it is stated that total quantities dumped or discharged in 1980 were about 2.3 and 1.2 million tons, respectively. These figures do not include waste from plants in Finland, Italy, Yugoslavia and the Eastern European countries. Neither is (the relatively modest) discharge of residual acid into Weser, FRG, included. The discrepancy between information given in the above report and data presented by Pickaver (1982) is, at least in part, due to the lack of common measure units. Moreover, Pickaver's table 1 wrongfully gives the impression that all wastes considered contain 23 % sulphuric acid, cf. Table 1.

Quantitative data available to the author with regard to the wastes mentioned in Table 1 are summarized in Table 2. It must be emphasized that the figures are approximate, that the waste amounts may have changed considerably with time and that different sources are not always in accordance.

To calculate the yearly byproduction of ferrous sulphate and sulphuric acid is only possible with information about the relative quantities of different raw materials used. Assuming a worst case, i.e. all sulphate process production based on Norwegian ilmenite, one gets yearly byproduction of the order 3.7 mill. tons pure $FeSO_4$ (corresponding to ~ 6.7 mill. tons of copperas or 1.3 mill.tons of iron). Byproduction of 100 % sulphuric acid will be of the order 4-5 mill. tons per year (taking into consideration that slag as raw materials results in more sulphuric acid waste than ilmenite). Considering the extensive use of other raw material than Norwegian ilmenite, the calculated amount of iron waste may represent an overestimation of about 50-100 %. To estimate how much of the waste which is dumped, respectively recycled or used in other ways, requires detailed information from the individual producers.

Table 2. Examples of approximate waste amounts from some titanium dioxide factories (cf. Table 1 for composition and concentrations of specific substances).

Factory	Quantity in 1000 tons per year	Recipient	Ref.
Titangesellschaft Nordenham, FRG	~650	Dumping site in German Bight	Weichart 1972
Titangesellschaft Nordenham, FRG	~7000-11000	Weser estuary	Wienecke 1982
Titangesellschaft, Leverkusen, FRG	~500	Dutch dumping site, North Sea	Composition: Kinne and Schumann (1968) and Kayser (1969) Quantity: Pickaver (1982)
N.L. Industries, Sayreville, USA	~2.900	New York Bight	Vaccaro et al 1982 Terminated 1982
Canadian Titanium Pigments, Varennes, Canada	~13.500	St. Lawrence River	ERCO and ECO-RESEARCH 1980
Toxide, Tracy, Canada	~5.000	St. Lawrence River	ERCO and ECO-RESEARCH 1980
Vuorikemia Oy, Finland	~2.800 - 3700	Bothnian Bay	Häkkilä (1978) Häkkilä et al.(1978)
British Titan Products England	~8.200	Humber estuary	Wilson and White (1974)
Kronos Titan A/S Norway	~6.100	Glåma estuary	Knutzen et al. (1974)
Du Pont Delaware, USA	~450	65 km south east of Delaware Bay	Pesch et al. (1974)

5. PHYSICAL AND CHEMICAL EFFECTS

The main effects are:

- acidification
- increased partial pressure of carbon dioxide
- elevated concentrations of metals, particularly iron
- precipitation of ferric hydroxide and increased turbidity
- oxygen consumption by oxidation of ferrous to ferric iron
- deposition and accumulation of ferric hydroxide on the shore and in sediments.

Freshwater recipients will also have a considerable increase in sulphate ions.

Often the precipitation will be followed by a marked change of colour from the greenish ferrous sulphate to the brown colour of ferric hydroxide precipitate.

5.1 Acidification

Acidification is undoubtedly one of the major factors behind negative effects observed in the laboratory and damage to recipient communities. In addition to the direct effect from sulphuric acid, the content of ferrous sulphate contributes to acidification or causes delayed neutralization in comparison with solutions containing equal concentrations of sulphuric acid. This is due to the alkalinity demand of ferrous iron when oxidized to the ferric state:

$$4\ Fe^{++} + O_2 + 2\ H_2O = 4\ Fe^{3+} + 4\ OH^-$$

$$Fe^{3+} + 3\ OH^- = Fe(OH)_3$$

Such "delayed" neutralization has been observed in bioassay with the waste water (Lassus and Maggi 1977).

Besides the amount and concentration of waste the pH conditions of receiving waters will depend on several factors: mode of discharge, water movement and buffering capacity.

By dumping in oceanic waters it appears that serious decrease of pH has been observed to be transitory and affecting limited water volumes, provided that rapid dilution is obtained by discharge into the wake water of a barge. At the National Lead dumping site in New York Bight, pH as low as 3.0 was recorded in the barge wake, rising within seconds to above 5.0, however. A pH of 7.0 or below was registered 7-900 m and about 3 min. behind the boat (dilution > 1 : 8000), and in isolated packets of water at a distance of 2500 m (Ketchum and Ford, 1948, Redfield and Walford, 1951). From the same site Ketchum (1974) states that pH was about 7.0 15 min. after passing of the barge, whereas EPA (1982) maintains that neutrality was reached within 5 min. Redfield and Walford (1951) calculated the water masses affected with pH 7.0 or below to be about 200 000 m^3.

Similar results are reported from the dumping site in the German Bight by Weichart (1972, 1975b, 1977). Typical pH values in wake waters after dumping were about 7.8 after 1 hour (dilution about 1 : 10 000), ~ 8.0 after 2 hours and above 8.1 after 5 hours, as compared with 8.2 - 8.3 outside the affected area. Yearly studies 1969-1974 gave no indications of a trend in the direction of increased acidity. Continuous monitoring of bottom water (~ 25 m) over a period demonstrated that the pH remained normal even under the wake when dumping took place (Weichart 1977).

At the dumping site in the Tyrrhenian Sea (Montedison waste, cf. Table 1) Archimbaud (1974) found an immediate lowering to pH 6.1.

By the pipeline discharge of a similar, but less acidic waste (cf. Table 1) into the very brackish water (5-6 o/oo S) of the Bothnian Bay, the primary diluted waste mostly floats along the bottom (Häkkilä et al., 1978). Secondary dilution depends on the shifting conditions of wind, stratification and currents. Thus packets of water with quite low pH may occasionally occur in a non foreseeable manner within a distance of 1.5-5 km from the outfall (Lehtonen 1976). Generally, however, pH below 6.0 is rarely observed farther from the source than 1-1.5 km (Lehtonen op.cit.). Dilutions above 1:1000 are required to establish pH close to neutrality (Lehtonen and Tuunainen 1974, Häkkilä 1978).

Two British factories discharge acid waste to the Humber estuary. The waste referred to in Table 1 is neutralized to pH ~ 6.5 and ~ 7.0 at dilutions 1:500 and 1:1000 in the brackish water (Wilson and White). At falling tide a pH just below 6.5 has been observed 1250 m from the outfall. The ratio of effluent discharge to mean freshwater flow is about 1:1000.

In the estuary of Glåma in Norway initial dilution with river water takes place before discharge, and a diffusor arrangement below the halocline ensures fairly rapid neutralization. Direct measurements of pH in the recipient are rather few, but acidic conditions below pH < 6.5 have not been observed (Arnesen 1969, Kristiansen 1970), and are less probable farther than 1 km from the outfall. Titration of the effluent with recipient water showed that dilution higher than about 1:500 would result in pH 6.5 or higher (Simensen and Liseth 1967, Kristiansen 1970). Theoretical calculations and rhodamine tracer studies indicated that the required dilution would be reached within a distance of less than 1 km (Simensen and Liseth 1967). Effluent discharge is less than 1:3000 of mean freshwater flow.

The St. Lawrence river in Canada receives two acid waste effluents (Table 1). The Tracy and Varennes effluents constitute less than 0.003 and 0.008 % of the river flow (ERCO and ECO-RESEARCH 1980). Marked acidification occurred only in relatively small water volumes (as compared to total flow) and was limited to the outfall side of the river. Decrease in pH of the river water was observed in packets of water up to 4-5 km downstream of the outfalls, but pH below 7.0 (dilution about 1:250) was not observed at distances above 300 m (ERCO and ECO-RESEARCH 1980).

5.2 Increased pressure of carbon dioxide

The relation between free carbon dioxide (gas), carbonic acid (dissolved), bicarbonate and carbonate is described by the equilibrium:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \text{ (minute amounts) } \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2\,H^+ + CO_3^{--}$$

The relation between free carbon dioxide, bicarbonate and carbonate in seawater is shown i Figs. 1-2. In contrast with the situation shown in the figures, the total content of carbonic acid and its salts is not changed by adding acid waste. Hence the increase in partial pressure of free carbon dioxide is limited. The speed of stripping of carbon dioxide to the atmosphere and the concomitant increase of pH depend upon aeration (as for instance observed in the laboratory by Kinne and Schumann, 1968); in practice upon the turbulence of the water.

5.3 Elevated iron concentrations in water

The other main component of the waste, dissolved ferrous sulphate is oxidized and precipitated as ferric hydroxide at pH 5.5-6.0 (Kristiansen 1970). As this pH mostly is reached few minutes after introduction of the waste into the recipient water (cf. above), dissolved iron most probably constitutes a minor part of total iron concentration except in the immediate vicinity of the outfall or closely behind a dumping barge. (The Finnish discharge to the Bothnian Bay may be an exception to this due to poor dilution conditions.)

In the German Bight Weichart (1972, 1975a) has observed 100 mg Fe/l at the immediate dilution of 1:500. About 7 and 2.5 mg Fe/l were observed about 1 and 2 hours after dumping and at dilutions of the order 1:10 000 and 1: 20 000. The highest concentration observed outside the visible waste cloud was 0.5 mg/l (Weichart, 1975a) corresponding to dilution of about 1: 100 000. Evidence of permanent elevation of iron concentration in large water volumes was observed by Weichart (1972 a,b) 5 months after start of the dumping. Iron concentrations were above 0.05 mg/l over a surface area more than 300 km^2, in contrast to a background level of 0.02-0.04 mg/l.

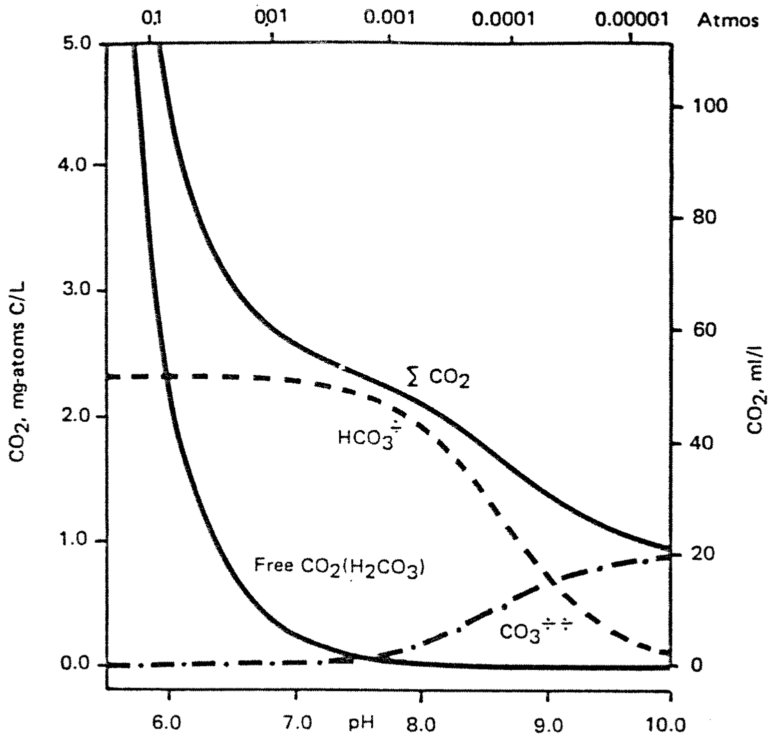

Fig. 1. Variation in total CO_2, free CO_2, $H_2CO_3^-$ and CO_3^{--} in seawater ($Cl = 19\ ^o/oo$, 20^oC) as function of pH and partial pressure of carbon dioxide. Modified after Sverdrup & al. (1942).

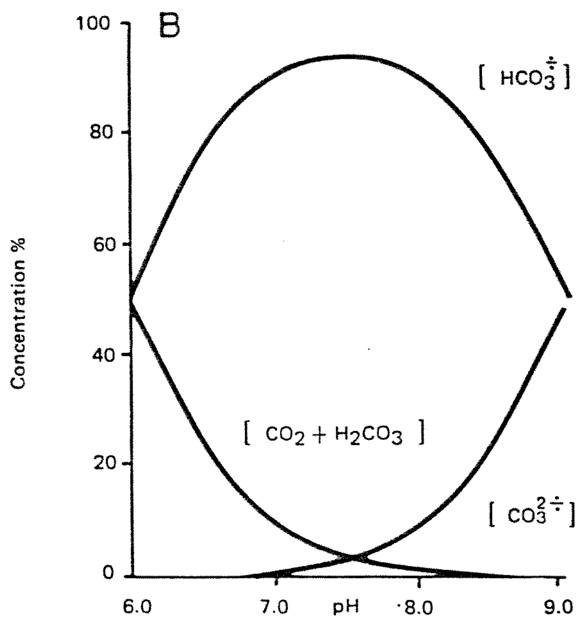

Fig. 2. Relative distribution between CO_2 $(+H_2CO_3)$, HCO_3^- and CO_3^{--} in seawater ($Cl = 19\ ^o/oo$, 25^oC) as function of pH (From Borowitzka and Larkum, 1976).

The long-term effect of waste disposal in this area has been confirmed by later studies (Weichart 1975a, Schmidt 1979). The latter author refers observation of iron concentrations above 0.2 mg/l in surface waters and about 0.7 mg/l at 30 m depth in the vicinity of the TiO_2 dumping site, less than 0.01 mg/l being in the dissolved state. For the water masses with permanently elevated iron concentrations Weichart (1975a) calculated that the total iron amount was equivalent to about one week's dumping. There were no indications, however, that the waters of the German Bight as a whole showed elevated iron concentrations (Weichart 1975a). In this connection it is worth mentioning that the daily dumping (above 90 t as iron per day) is of the same order of magnitude as the load of about 100 t/day from the rivers Elbe and Weser (Weichart 1975a).

Similar accumulation does not appear to have been observed in the neighbourhood of the New York Bight dumpsite of National Lead Industries, Sayreville (Redfield and Walford 1951, Ketchum et al. 1957, Vaccaro et al. 1972, Ketchum 1974). The calculations of Ketchum (1974) of the flushing time of Bight waters indicate that accumulation is not to be expected. After dumping in the propeller water of the barge the following dilutions and iron concentrations may be regarded as representative (Redfield and Walford 1951):

Time after passing of the barge	Dilution	Iron concentration in mg Fe/l
~ 3 min.	~ 1 : 1000	~ 30 mg/l
~ 5 min.	~ 1 : 4000	~ 8 mg/l
~ 2 hours	< 1 : 10000	< 3 mg/l

Ketchum (1974) reports even more rapid dilution: ~ 1:20 000 (1-2 mg Fe/l) within about 15 minutes.

At both the above dumping sites and in neighbouring water masses the details of the iron distribution will vary considerably with wind, currents and whether the water is stratified or turbulent. In particular, this has been observed in the German Bight (Weichart 1975a).

In the Bothnian Bay elevated iron concentrations (> 1 mg Fe/l) have been observed in the bottom water over a large total area, but in varying directions from the Vuorikemia outfall (Lehtonen 1975, 1976, Voipio and Niemistö 1975). According to Lehtonen (1976) such polluted waters have been found 10-15 km to the north and no less than 25 km to the west. Even if concentrations of 1 mg Fe/l are occasional and local there have been observed episodes with more than 100 mg Fe/l 4-5 km from the outfall (Lehtonen 1975, 1976). The same author states that near shore waters have experienced a doubling of the iron concentrations in the period 1964-65 to 1971-72 (Lehtonen 1975). Occasional upwelling of bottom water causes high turbidity and elevated iron concentrations in surface waters as well (Voipio and Niemistö 1975); concentrations reaching 0,4-2,2 mg/l and areas affected being up to a few km^2 (Lehtonen 1976).

In the Humber estuary (U.K.) dilution and shape of waste water plume shift markedly with rising and falling tides. In the fairly concentrated plume during falling tide, affecting a minor part of the river water, characteristic concentrations within the plume at 500 and 1000 m from the outfall were above 40 and 20 mg Fe/l, respectively at dilutions ~ 1-200 and ~ 1:400, (Wilson and White 1974). (At slack waters the effluent is held back around the outfall, but no values of pH or Fe-concentrations are given for these situations.)

In the Glåma estuary and the neighbouring Hvaler archipelago, Norway, iron concentrations have increased as a result of the Kronos Titan A/S waste water. Originally the waste amounted to more than 3 times the natural iron transport of the river (Arnesen et al. 1973). Later the waste iron load has been reduced by ca. 1/3 (E. Lund, pers. comm.). Concentrations of 0.5-1 mg Fe/l are common over the more than 40-50 km^2 of surface waters which are more or less permanently influenced by river water (Arnesen 1969, Knutzen 1970, Bokn et al. 1976). Outside the estuary proper concentrations above 1 mg/l have rarely been observed and are less probable farther from the outfall than 3-4 km (Bokn et al. 1976), and then in the mainstream of the freshwater. Later observations have confirmed that iron concentrations are elevated in the resipient water; further, that merely a minor fraction is in the dissolved state (J. Skei, personal communication).

No specific figures for iron concentrations are given in the report of ERCO and ECO-RESEARCH (1981) about the conditions downstream to the acid waste discharges into the St. Lawrence river. It may be deduced from dilution data, however, that iron concentrations higher than 1 mg/l will occur in the rather discrete waste plume or in packets of diluted waste at least 2-5 km from the outfalls.

Whereas the iron concentration has direct influence on water turbidity and amenities, elevation of other metal concentrations will be considered in connection with possible toxic effects.

5.4 Increased turbidity

Change of colours and increased turbidity have been observed as a permanent phenomenon around the dumping area in New York Bight (Ketchum and Ford 1948, Ketchum et al. 1958, Westman 1958, Vaccaro et al. 1972, Ketchum 1974). During the first years of dumping it was maintained that the effect was transitory (Ketchum and Ford 1948) and with no longterm effect on light transmission (Redfield and Walford 1951). Westman (1958) stated, however, that the area was permanently marked by the barging, and he indicated that in clear weather the old waste was visible over about 15 km. In an EPA working document (Anonymous 1982c) it is stated that turbid water is spread over a large area and remains visible several days after dumping. The same is experienced at another dump site on the East coast of USA (Reynolds, 1979). Ketchum and Ford (1948) found that in an area with old acid waste only 30 % of light absorption was due to phytoplankton, as compared with 60-80 % at two unaffected localities.

Generally, the waste water to a large degree remained in the upper part of the water column. Only in water without distinct stratification the waste penetrated to the bottom (Ketchum 1974).

The latter observation is in accordance with experience from the German Bight, and is explainable by the fact that the waste does not require dilution to more than about 1:250 (which takes place in seconds) before the specific weight is equivalent to the surrounding water (Weichart 1977). Thus the waste is prevented from rapid penetration of the pycnocline.

The precipitate is in stead dispersed in large volumes of water while slowly sinking. The sinking particularly takes place during calm weather and under destratified conditions (Weichart op.cit.). During turbulent conditions ferric hydroxide particles suspended over the sediment may again be brought to the surface (Weichart 1975a).

As mentioned before, rise of diluted waste to the surface is also experienced in the Bothnian Bay. This takes place during certain wind conditions, and the resulting brown coloured packets of surface water may cover a few km^2 (Lehtonen 1976).

Increased turbidity caused by ferric hydroxide precipitation has been more difficult to observe in the Glåma estuary. In part this is caused by the outfall arrangement aiming at entrainment of waste at intermediate depth. Another factor in this area is that once brought below the halocline the waste will not easily rise through the usually distinctly stratified water. Thirdly, due to natural high turbidity caused by muddy freshwater, and particulate matter from other industry, it is difficult to assess the role played by titanium dioxide waste. Influence on aesthetic amenities is more easily observed as a rust coloured deposit on the shores 4-5 km downstreams of the outfall (Bokn et al. 1976).

An important aspect of the ferric hydroxide flocs is their deposition on fishing nets. This has seriously hampered fishing in the sea area affected by the Finnish factory. Nets and traps have often been heavily covered by deposits within 3-4 km from the outfall (Lehtonen 1976). Reduced catch per man power unit and partial stop of fishing have caused considerable economic loss to fishermen of the area (Lehtonen 1975, 1976). The iron content of the deposit showed large variation, with an extreme of 37 % (Lehtonen 1976). Deposition of ferric hydroxide on fishing nets and traps has also been observed in the Glåma estuary, but in a minor scale.

5.5 Waste accumulation on the shore and in sediments

The brownish deposit on the shores of the Glåma estuary has already been mentioned. Similar adverse effects have not been reported from other recipient areas. It is probable, however, that the phenomenon also occurs in connection with discharge to other river or estuarine environments (e.g. Humber, St. Lawrence, Seine). From dumping sites in the ocean there is no evidence that the waste reaches the coast in such quantities that shore amenities and communities of organisms are affected.

From the Finnish factory near Pori the waste mainly flows as a stream along the bottom towards the deep water of the Bothnian Bay (Isotalo and Häkkilä 1978). Nevertheless, a large area is characterized by elevated concentrations of titanium and iron in the surface sediments in the vicinity of the outfall (Voipio and Niemistö 1975, Häkkilä et al. 1978). Also zinc and vanadium show elevated levels (Isotalo and Häkkilä, 1978). According to a map presented by Häkkilä et al. (op. cit.), 3-4 km^2 in the immediate vicinity of the outfall is termed "TiO_2-mud", and a more distant area of about 120 km^2 is marked by ferric hydroxide precipitate. Asplund et al. (1980) found considerably elevated sediment levels of cadmium, zinc and lead in the vicinity of Pori as compared with a reference area. It is somewhat uncertain, however, to what extent this can be attributed to titanium dioxide waste. According to Lehtonen (1976) the acid waste load represents about 50 % of the zinc and less than 1 % of the cadmium coming from the polluted river Kokemäenjoki.

In the Glåma estuary and the Hvaler archipelago of Norway moderate increase of iron concentrations was recorded in the uppermost cm of sediments (Arnesen et al. 1973) shortly after start of waste discharge. Recent studies confirm elevation of iron and titanium, possibly of other metals too (K. Næs and J. Skei, pers. comm.). Investigation of bottom fauna has shown that, at some of the affected localities, the brownish topmost sediment layer is more gelatinous and adhesive than normally (B. Rygg, pers. comm.). More definite conclusions about degree and areal extent of the above mentioned effects must await detailed analysis of the material.

Analysis of sediment samples of the Weser estuary revealed no iron accumulation (Wienecke 1982). Taking into account the comparatively dilute character of this residual acid waste (< 80 mg Fe/l, cf. Table 1), accumulation is rather not to be expected.

From the Humber estuary Wilson and White (1974) report the occurrence of a ferric hydroxide crust close to the point of discharge from British Titan Products and the discoloration of surface sediments several hundred meters to both sides of outfall pipe. However, elevated concentrations of waste constituents have merely been found close to the outfall.

No clear enrichment of iron or other metals has been observed in the sandy sediments of the New York Bight dumping area (Corwin and Ketchum 1956, Vaccaro et al. 1972, Anon. 1982a); the latter referring to reports by the National Oceanic and Atmospheric Administration of the U.S. Theoretical considerations of the flushing time of water in the affected area, as well as the sedimentation characteristics of the waste, support the plausibility of no accumulation (Ketchum 1974). In some contrast to this, Lear et al. (1974) found indications that iron, manganese, chromium, zinc and some other metals were deposited in sediments at the Du Pont dump site outside Delaware Bay. Significant correlation was found between content of iron and the other above mentioned metals.

In the German Bight Weichart (1972, 1975a) reports no accumulation of iron in bottom sediments 5 and 16 months after dumping began about 14 nautical miles NW of Helgoland. Rachor (1972) reports a loose mass of hydroxide flocs floating over the sandy sediments, but no crust on the sediment surface. The same observations are referred in Rachor and Dethlefsen (1974). Unfortunately, more recent data have not been published.

5.6 Oxygen consumption

According to the equation

$$4\ Fe^{++} + O_2 + 2\ H_2O = 4\ Fe^{3+} + 4\ OH^-$$

the oxidation of 1 g atom ferrous iron requires 1/2 g atom oxygen, i.e. for every g of iron, it is necessary with about 0.14 g oxygen. Thus the saturation content of 7-14 g oxygen in one m^3 of water will be enough to oxidize 50-100 g ferrous iron. Assuming a total yearly waste production of close to 4 mill. tons of ferrous iron (cf. chapter 1) the chemical oxygen demand would be met by the oxygen content of a water mass of 1000 km^2 with a mean depth of about 70 m or about 0.3 % of the world's largest freshwater lake. Consequently, oxygen deficiency should only be a local problem or occur in low capacity recipients.

Calculations and observations from ocean dump sites confirm the above reasoning (Ketchum and Ford 1948, Weichart 1972, Vaccaro et al. 1972). In the dumping area for waste from Montedison, however, Archimbaud (1974) registered a modest oxygen deficiency of 10-15 %. The only acid waste recipient reported to have definite oxygen problems is the bottom water in the surroundings of the Finnish TiO_2 factory. Lechtonen (1976) describes the oxygen conditions as generally satisfactory most of the time, but with episodes of deoxygenated bottom water up to 10 km from the outfall. It should be added that a considerable COD load comes from a pulp waste polluted river draining to the same area. There are also some indications of intermittent oxygen deficiency in the sediments of local depression basins in the Glåma estuary (B. Rygg, pers. comm.). However, the relative role played by ferrous iron waste versus organic loading is uncertain.

6. WASTE ACCUMULATION IN BIOTA

There are few accounts of metal registrations in organisms from the German and American dump sites, but the results so far indicate no or merely uncertain accumulation (Rachor 1972, Greig et al. 1977, Pesch et al. 1977, Reynolds 1979). Pesch et al. (1977) reported increased vanadium concentrations in the sea scallop *Placopecten magellanicus* from sampling stations south of the Du Pont dump site off Delaware Bay. The augmentation was about 2-3 times, as compared with levels in scallops collected from stations presumed to be less affected. It should be added, however, that the geographical distribution of elevated vanadium concentrations neither was consistent from year to year, nor did the vanadium levels correlate well with other tracer substances for the waste (iron, titanium, chromium).

Karjala (1980) compared the metal content of flounder (*Platichtys flesus*) and the bivalves *Mytilus edulis* and *Macoma baltica* from the Finnish recipient area with a reference locality. With large variation between individuals the mean concentrations of metals in fish from several stations within or near the acid waste polluted area were about ten times higher for lead and copper and two times higher with respect to zinc and cadmium. In contrast, metal levels measured in the two bivalves showed no or insignificant increase. Unfortunately no data are available respecting concentrations in animals of the main constituents of the waste. It is also possible that the polluted waters of the river Kokemäenjoki may contribute to the elevated lead and copper levels. Some doubt as to the full validity of the results reported by Karjala (op.cit.) is caused by the unusually high metal concentrations found in mussels from the reference area.

ERCO and ECO-RESEARCH (1980) observed accumulation of titanium and nickel in the adductor muscle of the mussel *Elliptio complanate* downstream to the Varennes discharge to the St. Lawrence river. Concentration factors were calculated to 36 and 370, respectively for Ti and Ni.

Elevated concentrations of iron, manganese, zinc and titanium, possibly also of chromium and vanadium, have been recorded in the brown alga *Fucus vesiculosus* in an area 6-10 km south of the Kronos Titan discharge in the Glåma estuary (unpublished). Conservative estimates indicate increases of the order 10-20, 5-15 and 5 times the normal concentrations of iron, manganese and zinc, respectively. For titanium there is as yet no published data basis for comparison, but the concentrations found in bladder wrack from more distant locations in the area indicate a minimum increase of 5 times the background level. More moderate increases of iron and manganese (ca. 2-4 x) were recorded about 15 km from the factory. Some reserve with regard to causal relations must by taken due to heavy influence from freshwater rich in iron (on average about 150-200 µg/l). On the other hand, manganese concentrations of the river water are moderate.

The indications of metal pollution in the Hvaler archipelago were less clear from analysis of mussels *(Mytilus edulis)*. Elevated levels were recorded, however, particularly for titanium, to a minor degree for manganese. Comparable data are sparse, but assuming wet weight basis for the figures from accumulation tests conducted by CERBOM (France) and published in a report from the Commission of the European Communities (1975), a minimum of 5 times the background concentration of titanium was indicated. Observed iron concentrations were in the upper part of or slightly above the normal range.

Results of experimental accumulation and biomagnification studies have been reported by the Commission of the European Communities (1975) and by Maggi and Lassus (1974). In the food chain experiments performed by the latter, no metal accumulation was observed, except for iron flocs in the intestine of *Artemia*. According to the Commission report (op. cit.) the concentration factors observed for titanium and vanadium were lower in blennies (fish) than in the preceding link of the food chain. Consequently, no biomagnification was observed.

In his experiments with iron flocks and mussels Winter (1972) observed concentrations up to 9 times the control value. These mussels experienced considerable weight loss, however, and measured on individual in stead of wet weight basis, the increase was merely 3 times. Thus it may appear from these tests that any gross accumulation of iron in mussels are rather not to be expected. (Cf. the modest if any increase of iron in mussels sampled from the outer Glåma estuary.)

7. BIOLOGICAL EFFECTS

As is evident from the account of physical and chemical effects of acid waste the affected biological communities may be exposed to a variety of stress factors: decreased pH, elevated CO_2 partial pressure, toxic concentrations of iron and perhaps other metals, precipitation and flocculation of iron hydroxide with associated metals, increased turbidity and concentration of particulate matter, poorer light conditions, impaired substrate conditions or smothering by particles. The variety of possible mechanisms may complicate the design of bioassay procedures and often makes it difficult to interpret results from laboratory as well as field observations. With respect to toxic effects from metals, these will depend upon both concentration and chemical form.

7.1 Phytoplankton and primary production

Kayser (1969) tested the influence of waste water from Titangesellschaft m.b.H., Leverkusen (cf. Table 1, second column) upon the growth of the two marine dinoflagellates *Ceratium furca* and *Prorocentrum micans*. The tests were performed under both static and semi-continuous conditions. The static tests were conducted with diluted media which were newly made or 24 hours old. The former represents an additional stress in two ways: Miniumum initial pH and precipitation of ferric hydroxide. In old waste water dilutions pH had stabilized at a somewhat higher level and the flocculation had taken place when the inoculum was added. In the semi-continuous cultures part of the waste water medium was renewed daily by the volume required to keep constant cell density in the control culture. The various experiments lasted 15-35 days, and the dilutions tested were 1:2500 to 1:100000.

The experiments showed that lethal concentrations were about 1:2500/3000 and 1:3500, respectively for *Prorocentrum* and *Ceramium*. However, there was some difficulty in establishing a treshold of lethality, because in som cases a few cells were alive, but inactive, at the end of the experiments.

Some negative effects on cell division were observed during the first days in all the concentrations tested. Except in the higher concentrations the cells regained their vitality and showed division rates close to that of the control culture. For *Prorocentrum micans* there was some variation in results with the different test procedures, but in one of the"chemostat"assays effects were marked in dilution 1:25000/32000. Under similar conditions *Ceratium furca* showed reduced division rates and yield at 1:50000. It should be added that the effect in most, but not all cases, increased consistently with waste load. Aging of the waste appeared to be of less importance. On the other hand, it was evident that some selection or adaptation took place in the cultures, resulting in less pronounced differences of effects towards the end of the experimental period compared to the initial phase.

Experiments with the Haptophycean alga *Phaeocystis poucheti* gave evidence that this species was less sensitive to the acid waste than the above mentioned dinoflagellates (Kayser, 1970). Lethal dilution was as low as 1:2250, and pronounced negative effect on multiplication rate was not evident in dilutions above 1:5000. Possibly, the explanation for this difference is the protective effect from the gelatinous membrane around the colonial stage of *Phaeocystis*.

Ketchum et al. (1957) were among the first to test the effects on primary producers. They used the Chlorophycean *Dunaliella euchlora*, which was cultured in water sampled in the barge wake at the dumping site of National Lead in the New York Bight. Total iron concentrations ranged from 0.4 to 35.5 mg/l, whereas pH in all media was about 7.9. In the latter concentration there was no growth, and negative effects were observed down to 2.7 mg Fe/l. Assuming iron concentration in the waste as given by Grice et al. (1973), the above values correspond to waste dilutions about 1:1000 and 1:12000, respectively.

With waste water from the same factory Vaccaro et al. (1972) did not observe any effects on growth or diversity in a mixed culture of diatoms when the iron concentration was 3.25 mg/l (dilution about 1:11000).

Lassus and Maggi (1974) refer from experiments conducted by CERBOM that the effluent of Montedison (cf. Table 1) was toxic to the diatom *Asterionella japonica* in dilution 1:2000. They give no data for waste concentrations from their own experiments with phytoplankton, but attribute most of the observed toxic effects to decreased pH. Division rate in *Phaeodactylum* was reduced 10, 27 and 55 %, respectively at pH 7.3, 6.6 and 5.6.

In another paper Maggi and Lassus (1974) state that they have observed reduced growth in cultures of the diatoms *Phaeodactylum tricornutum* and *Skeletonema costatum*, the chlorophycean *Dunaliella tertiolecta* and the haptophycean *Isochrysis galbana*. The effect was evident when initial pH was 6.0 in the three different waste media. Corresponding iron concentrations of these were 22, 25 and 8.7 mg Fe/l, respectively for waste from Montedison, Thann et Melhouse and Tioxide (cf. Table 1).

Arnesen et al. (1973) found that growth of *Phaeodactylum* decreased in Kronos Titan A/S waste in dilution 1:500, corresponding to an iron concentration of 8 mg/l. (The iron content of undiluted waste was in this case found to be 30 % higher than stated in Table 1.)

To facilitate the comparison of observations from different studies, the above results have been compiled in Table 3, together with data on dilution, pH and total iron concentrations. It should be stressed that the test procedures and experimental conditions vary to an extent which it is not possible to express in a concise way. Taking pH as an example, this factor usually has risen during the experimental period. This is expressed by a parenthesis around extreme, incipient values. In several cases it has been necessary to calculate the tabulated data, sometimes based on the somewhat dubious assumption that the waste in question has a constant composition or that the waste used in experimental studies has the same composition as given in other papers than those referred to (compare references in the Tables 1 and 2).

With this reservation in mind, it appears that deleterious effects on phytoplankton are associated with pH below about 7.0 - 7.5 and/or iron

Table 3. Summary of results and experimental conditions in terms of approximate pH and total iron concentrations (mg/l) in tests with acid waste and phytoplankton species. (Cf. text for further information. Note that the dilution figures refer to waste of different composition, cf. Table 1.)

Test organisms	Lethal effects			Sublethal effects			References
	Waste dilution	pH	Iron conc.	Waste dilution	pH	Iron conc.	
Prorocentrum micans	~ 1:3000	(5.9)[2] 6.7-7.0	28[1]	1:32000	(7.2)[2] 7.7-8.0	2.6[1]	Kayser 1969
Ceratium furca	~ 1:3500	~ 7.0	24[1]	1:50000	7.9-8.1	1.7[1]	
Phaeocystis poucheti	1:2250		38[1]	1:5000		17[1]	Kayser 1970
Dunaliella euchlora	1:1000[1]	~ 7.9	35.5	1:12000[1]	7.9	2.7	Ketchum et al. 1957
Asterionella japonica				1:2000		24[1]	CERBOM ref. by Lassus and Maggi 1974
Various, see text					6.0 → ?	9-25	Maggi and Lassum 1974
Phaeodactylum tricornutum				1:500	?	8	Arnesen et al. 1973

1) Calculated for this review

2) Incipient, short-lasting values

concentrations about 2 mg/l or higher. Cause-effect relationships are difficult to resolve as long as the relative importance of iron (and other metals) versus acidification has not been elucidated in tests separating these factors.

ERCO (1982) referring to studies not available for this review (ERCO 1978, 1981) mention a 96 hour environmentally protective concentration of 20 ppm waste from NL Industries, Sayreville, with regard to *Skeletonema costatum*. Harmful concentrations are not cited. (Environmentally protective concentrations are concentrations at which no sublethal effects have been observed during a specified period of time.) 20 ppm NL Industries waste (cf. Table 1) corresponds to an iron concentration of less than 1 mg/l. Consequently, if effective concentrations have been close to this level, there are indications that the waste is even more hazardous than it appears from the results referred to in Table 3.

To the author's knowledge there are no published data from in situ observations of primary production. According to EPA (Anonymous 1982c) no effects have been observed in primary production studies at the New York Bight dump site in spite of the theoretical calculations of Ketchum et al. (1958), indicating about 50 % reduction of the production potential in the area affected by turbid water after barging. Vaccaro et al. (1972) deduced from oxygen saturation data in the same area that interference with primary production was none or insignificant.

7.2 Zooplankton

Possible effects on zooplankton other than fish larvae (see below) do not seem to have attracted much interest in connection with acid waste. A summary of accessible data from experimental work has been summarized in Table 5.

Introductory experiments with N.L. Industries waste were conducted by Ketchum and Ford (1948, also in Redfield and Walford, 1951). The tests were performed with a mixed population of plankton. In seawater diluted waste corresponding to 2-26 mg Fe/l and initial pH 7.4 - 5.7 the animals were first paralyzed. However, in concentrations of iron up to 10 mg/l they regained their mobility within 2-3 minutes. The observation time was limited to 5 minutes.

Later experiments with cladocerans (Ketchum et al. 1958) demonstrated the possibility of interference of iron hydroxide particles with feeding. After 12 hours in water with a high content of such particles the guts were filled, but the material was also readily excreted, seemingly with no harm caused. The same authors have observed high iron content in the intestine of planktonic crustaceans collected in the screw water of a dumping barge (Ketchum et al. 1957, 1958).

Apparently no harm from iron flocs in the intestine was also reported by Grice et al. (1973), but the phenomenon deserves special consideration in long-term tests, as has been done for common mussels (Winter, 1972, see below).

Vaccaro et al. (1972) found no toxic effects to fertile females of the copepod *Pseudodiaptomus coronatus* of the same waste in dilutions $1:10^5$. One order of magnitude higher waste concentrations gave marked effects - failure of hatching, increased mortality of larvae, and delayed maturation. Theoretically, a dilution of 1:10000 of this waste should correspond to about 3.3 mg Fe/l, but this is uncertain because the test medium was filtered. (In an introductory assay with unfiltered waste the surface and appendages of the crustaceans were covered by a brown precipitate, and it was observed a high mortality of nauplii.)

In an experiment aiming at the simulation of recipient conditions in the screw waters of dumping barges Grice et al. (1973) tested the effect of the same waste upon the copepod *Calanus finmarchicus*. All of 10 individuals survived the treatment, which consisted of dilution 1:500 (pH 3.0) for 3 minutes, 1:1000 (pH 5.5) for 3 minutes, 1:3000 (pH 6.5) for 5 minutes, followed by transfer to filtered seawater. However, one specimen was immobile and three showed abnormal swimming behaviour 30 minutes after test start, and two still had deviating behaviour after 3 hours. With transfer directly from 3 minutes stay in diluted waste to seawater, negative effects were observed for dilution 1:500, but not for 1:1000 or higher (normal behaviour after 10 minutes).

In 24 hours tests performed by the same authors, 30 % of individuals of *Pseudocalanus* sp. died in dilution 1:5000, 70 % of *Calanus finmarchicus* in 1:2500 and 80 % of *Temora longicornis* in 1:3000. Both the latter two sustained dilution 1:4000 (pH 6.6). In a 48 h experiment with *Temora* to test the effect of acidification alone, this species sustained pH 6.0 but died at pH 5.5. Partly neutralization of the waste indicated the important role of low pH in toxicity. *Calanus finmarchicus* then sustained 24 hours in dilution 1:250 (pH 7.4) but 60 % of the animals was dead after 6 days. In the higher dilution (1:500 - 1:8000) only one of 32 specimen died during the same period.

Finally, Grice et al. (op.cit.) demonstrated the failure of reproduction in *Temora longicornis* at dilution 1:4000 (pH 6.6). Lower than control results was also observed in 1:1:5000 (pH 6.9), whereas the production of nauplii was normal in dilution 1:6000.

Some of the studies with NL Industries and Du Pont waste mentioned by ERCO (1982) have not been available for the present review. Environmentally protective concentrations (cf. chapter 7.1) are claimed to be > 8 ppm of NL Industries waste in 96 hours for the mysid shrimp *Mysidopsis bahia* (ERCO, 1978, 1981) and 75 ppm in 672 hours for the same species in Du Pont waste (Falk and Philips, 1977). Corresponding iron concentrations would be respectively > 0.3 mg/l and about 3.2 mg Fe/l.

Maggi and Lassus (1974) performed 96 hours tests with the crustacean *Artemia salina* in various concentrations of waste from the three factories Montedison, Thann & Mulhouse and Tioxide. The iron concentrations of the three waste waters deviate slightly from the figures in Table 1 (see below). Assuming that above 10 % mortality represents a significant difference from the control, adverse effects were observed in the following dilutions: 1:5000 (12 % mortality), 1:500 (16 %), 1:2000 (15 %); the respective wastes listed in the same orders as the factories above. Supplementary tests with only sulphuric acid added indicated that pH was not the only factor responsible. In some cases higher death rate was observed in waste media with pH so high as to cause no harm in the experiments with sulphuric acid alone. In the latter tests pH 5.5 - 7.5 (0-4 hours) resulted in a death percentage of 34 % whereas pH 5.8 - 7.7 appeared to have no effect (compare Table 4).

Somewhat contradictory to the above results the same authors in another study (Lassus and Maggi 1974) were not able to demonstrate any mortality or harm to larval development in *Artemia* from dilutions higher than 1:1000 for Montedison waste or 1:250 for the Thann et Mulhouse effluent. Nauplii adapted rapidly and thrived well in media with pH above 5.5. The results of tests with *Artemia* and other organisms in Montedison waste reported to the Commission of the European Communities probably refer to the same experimental work as reported by Lassus and Maggi.

In their comprehensive study on larval development in the decapode *Palaemon serratus* Lassus and Maggi (1977) have used the same wastes as in the *Artemia* experiments. According to their own analysis the wastes were characterized by the below concentrations in mg/l. (Compare Table 1 with the composition as given by the respective companies.)

	H_2SO_4	Fe	Zn	Cu	Cd	Hg
Montedison	$147 \cdot 10^3$(3N)	$44 \cdot 10^3$	10	0.4	0.6	$4 \cdot 10^{-4}$
Thann et Mulhouse	$35 \cdot 10^3$	$12.5 \cdot 10^3$	103	2.3	0.4	$<5 \cdot 10^{-5}$
Tioxide	$102 \cdot 10^3$	$4.7 \cdot 10^3$	11	0.1	0.1	$<4 \cdot 10^{-5}$

These authors also used media with only ferrous sulphate or sulphuric acid added in concentrations corresponding to the tested waste dilutions. The experiments were performed over 30-60 days, with renewal of (mostly fresh) media (and concomitant decrease of pH) every 48 hours. pH was measured daily and in addition to mortality, several aspects of larval development were observed.

Unfortunately, interpretation of the results from these thorough studies was made somewhat difficult by large variation of mortality in the control cultures. Nevertheless, Lassus and Maggi were able to conclude that the three waste waters had toxic effects in the dilutions given in Table 4. They also concluded that the observed harmful consequences were associated either with iron concentration above 30 mg/l (weakly acid ferrous sulphate solution) and/or repeated short time exposure to pH 6.0 or below. At the same pH, mortality was less in cultures in which pH rose comparatively rapidly after the initial decrease subsequent to renewal of medium. The higher the concentration of ferrous sulphate, the slower neutralization took place. According to the authors there were no indications that other metals than iron played a part in the toxicity of detrimental concentrations.

Table 4. Summary of results and experimental conditions (approximate pH and total iron concentrations in mg/l) from tests with acid waste and zooplankton species. (See text for further explanation. Note that the dilution figures refer to waste of different composition, cf. Table 1.)

Test organism	Increased mortality			Sublethal effects			References
	Waste dilution	pH	Iron conc.	Waste dilution	pH	Iron conc.	
Pseudodiaptomus corronatus	1:10000		3.3.	1:10000	7.6	3.3[1,2]	Vaccaro et al. 1972
Calanus finmarchicus	1:2500	6.7[3]	12[1]				
Temora longicornis	1:3000	6.4	10[1]	1:5000	6.9	6[1]	Grice et al. 1973
Pseudocalanus sp.	1:5000	6.7	6[1]				
Calanus finmarchicus	1:250[11]	7.4	120[1]				
Artemia salina	1:5000[4] 1:500[5] 1:2000[6]	6.3-7.8[7] 5.7-7.4[7] 6.8-7.9[7]	8.6 25 2.2	1:1000[4] 1:250[5]			Maggi and Lassus 1974 Lassus and Maggi 1974
Palaemon serratus	1:2000[4] 1:500[5] 1:900[6]	5.8-7.0[8] 5.8-7.2[8] 6.0-7.5[8]	22[1] 25[1] 5.3[1]	1:1000[9]	6.2-7.6[8]	4.7	Lassus and Maggi 1977
Artemia salina				1:500	~7.0(?)[1]	16[1]	Wilson and White 1974
Daphnia magna	1:105[10] 1:480[10]	~6.2-7.2	~ 4[1] ~ 2.7[1]				ERCO and ECORESEARCH 1980

1) Calculated for this review
2) Probably lower concentration due to filtration of waste medium
3) pH 6.1 in 1:2000 and 6.7 in 1:5000 of the same experiment series
4) Montedison waste
5) Thann et Mulhouse waste
6) Tioxide waste
7) pH development, 0-4 hours
8) pH variation during the experiment
9) Effects on number of metamorphoses and number of moults before metamorphosis
10) 48 hours LC_{50} for respectively Varennes and Tracy waste
11) Partly neutralized waste

Wilson and White (1974) reported retarded growth of *Artemia* nauplii in dilution 1:500 of the effluent from British Titan products, corresponding to 16 mg Fe/l and a minimum pH of about 7.0.

The only tests conducted with freshwater zooplankton appear to be the experiments reported by ERCO and ECO-RESEARCH (1980) concerning the effluents from the Canadian titanium dioxide factories. The iron concentrations in the waste used in the tests varied between 400 and 730 mg/l (Varennes factory) and ca. 900 and 1250 mg/l (Tracy factory). 48 hours LC_{50} for the water flea *Daphnia magna* was respectively 1:105 and 1:480 (95 % confidence interval 1:100 - 1:50 and 1:330 - 1:1000). In the tests with 10 ppm Varennes, waste pH rose from 6.2 to 7.2 in the course of 48 hours.

From the summary Table 4 it is seen that with one exception there is rather good agreement between tests performed with different wastes, supporting the assumption that pH and iron concentrations are the key factors to be considered when judging cause and effect relations. From the zooplankton studies, waste dilutions giving pH lower than 6.5-7.0 together with iron concentrations above ca. 2 mg/l, appear to be definitely hazardous.

Observations of zooplankton in recipient areas are few. Neither in studies by Ketchum et al. (1958) and Vaccaro et al. (1972), nor in the thorough investigations by Wiebe et al. (1973), harm to zooplankton communities was observed.

7.3 Benthic organisms

For strict freshwater environment the only information available is the results from tests performed by ERCO and ECO-RESEARCH (1980). With Varennes waste water and the amphipod *Gammarus fasciatus* they observed a 48 hours LC_{50} of 18000 ppm, i.e. dilution 1:55 and iron concentration ca. 10 mg/l.

In contrast, many brackish and salt water species have been tested. In particular, many tests have been conducted to throw light upon recipient conditions in the vicinity of the Finnish factory in the Bothnian Bay. Bagge and Ilus (1975) demonstrated rather high tolerance for acid iron waste with short time exposure. The bivalves *Mytilus edulis* and *Macoma baltica* and the isopod crustaceans *Asellus aquaticus* and *Mesidotea entomon* were among the most tolerant. More than 50 % of the individuals of these species survived 24 hours in pH 2.4 - 2.7 (*Mytilus* and *Macoma*) or 3.5. The respective iron solutions were about 450 mg/l (*Mytilus*), 150-230 (*Macoma*) and 45-50 mg Fe/l for the isopods. (The iron content of the waste used by Bagge and Ilus was only about 1/5 of what is stated in Table 1.) Other crustaceans (*Neomysis integer, Gammarus salinus, Pontoporeia affinis* and *P. temorata)* were more sensitive, sustaining pH 4.5 - 5.5 and iron concentrations about 13 - 17 mg/l. The authors emphasize, however, that the test period was too short for any conclusions about tolerance limits.

In the more recent studies by Häkkilä (1978) the short-term high tolerance of *Macoma baltica* was confirmed, as the 96 hours median tolerance limit of this species was determined to be dilution 1:70 of the waste water (cf. Table 1). Further, the results for the crustaceans *Gammarus* sp. and *Pontoporeia affinis* revealed little difference between short-term (24 h) and long-term (16-24 days) median tolerance limit. The tolerance limit of *Macoma*, however, decreased considerably with time, TL_m reaching dilution 1:300 after 15 days, as compared to 1:550 for the most sensitive among the crustaceans. Approximate iron concentration and pH values corresponding to the above mentioned test solutions are listed in Table 5.

Häkkilä also performed tests with pure ferrous sulphate and sulphuric acid solutions, finding the 48 hours median tolerance limits of *Gammarus* sp. and *Idotea baltica* to be respectively pH 5.0 and 4.8 and ~ 90 mg Fe/l and ~ 35 mg Fe/l. Due to the alkalinity demand of ferrous sulphate these two iron concentrations were associated with pH 6.0 and 6.6. Comparative survival tests with *Gammarus* in different concentrations of ferrous sulphate and sulphuric acid also pointed to acidity as the main noxious factor. The author observes, however, that after an initial top in mortality, followed by a decrease, it tended to increase again towards the end of the experiments. This may be explained as a delayed effect of stress from low start pH or it may be due to other stress factors.

Häkkilä noted that the surface of test animals, particularly the gills, was covered by iron hydroxide precipitate, which also filled the intestine.

Halsband (1968) concluded after short-term tests with several species of fish and invertebrates (*Tubifex* sp., *Gammarus* spp. and *Crangon vulgaris*) that adverse effects of recidual acid were unlikely in dilutions above 1:40. Unfortunately he does not specify the composition of the waste. The term "recidual" acid ("Restabwasser"), used in the annexed discussion of the paper, indicates, however, that the waste concerned is of the same character which at present is discharged to the river Weser (Wienecke 1982). If so, the safe limit indicated by Halsband (op.cit.) corresponds to an iron concentration of about 1-2 mg/l.

Long-term tests with the molluscs *Mytilus edulis* and *Littorina littorea*, the shore crab *Carcinus maenas* and the polychaet *Arenicola marina* showed median lethal threshold dilutions of 1:125 - 1:500 (Wilson and White 1974), equivalent to about 25-100 mg Fe/l and initial pH below 4.0 (1:125) or about 6.5 (pH conditions have not been specified by Wilson and White but approximate pH may be derived from their Figure 1). *Mytilus* and *Arenicola* were least and *Carcinus* most tolerant in exposures lasting more than 10 days. Cage studies in the recipient with the brown shrimp *Crangon crangon* resulted in increased mortality at distances from the outfall corresponding to periodic exposure to dilutions about 1:350. From further experiments with *Crangon* Wilson and White found that the waste's harmful effects probably were attributable to its acidity.

In their 96 hours lethality tests with several marine shallow water species with waste from Montedison, Thann et Mulhouse and Tioxide (cf. Table 1) Maggi and Lassus observed considerable mortality in the following dilutions (mentioned in the same order as the above producers): 1:1000 (pH 3.3), 1:250 (pH 3.4) and 1:250 (pH 2.8). By doubling these dilutions no differences from the control cultures were found. In the worst of these cases (Tioxide 1:250), pH developed from 4.9 to 6.2 in the course of the experiment. Even in the mortal concentrations the bivalves

Cardium edule and *Mytilus edulis*, the snails *Littorina littorea* and *Purpura (Thais) lapillus* and the hermit crab *Clinaparius misanthropus* survived for 96 hours, but in an immobilized state. In tests with pure sulphuric acid in salt water no increased death rate was observed in media with pH interval 5.5 - 7.5 (respectively start and end of tests of 96 hours duration).

Tests with benthic organisms and Montedison waste have been conducted by Centre d'Etudes et de Recherches de Biologie et d'Oceanographie Medical (CERBOM). The following account of these experiments has been taken from a Commission of the European Communities report (1975). When calculating iron concentrations for Table 5 it has been assumed the same iron content of the waste as referred to in Table 1. For the brown shrimp *Crangon crangon* a dilution of 1:1000 was toxic, whereas the bivalves *Ostrea edulis, Cardium edule, Mytilus edulis* and the snail *Littorina littorea* survived this treatment. Toxicity thresholds were determined to be 1:8000 for *Mytilus edulis* and 1:2000 for the polychaet *Nereis diversicolor*.

The above mentioned works of Wilson and White (1974) and Maggi and Lassus (1974) both are somewhat difficult to compare with other results in terms of acidity conditions and iron concentrations. Wilson and White present their results only by means of response curves, not giving explicit data for pH and iron concentrations. Thus the figures in Table 6 must be taken with some reserve. With respect to Maggi and Lassus (op.cit.) the interval between effective and not effective waste concentrations has been too large to indicate threshold values.

Winter (1972) conducted long-term studies (several months) with the common mussel *(Mytilus edulis)* exposed to flocs of ferric hydroxide. 0.4-4.0 mg Fe/l was given to the mussels three times daily, with change of medium every second day. Both increased mortality and weight loss were observed, even at the lowest iron dose. 1 mg Fe/l caused weight reduction of 40 % after 3 months as compared with 10 % increase in the control mussels. The respective death rates were 75 % against 10 %. Production of pseudofeces increased with increasing amounts of iron flocks and Winter suggested that the adverse effects were caused by interference with food uptake and through extensive loss of organic material from excretion of mucus. The concentration of iron in this experiment is difficult to compare with the other works. Aplication of iron hydroxide three times daily makes it probable that iron concentration increased during the two days between renewal of the medium.

Data for the acid iron waste tolerance of benthic algae are virtually non existant. In experiments with the low salinity tolerant rhodophycean *Ceramium strictum* Arnesen et al. (1973) were unable to demonstrate any adverse effects upon growth or paraspore reproduction in dilutions of Kronos Titan waste down to 1:500 (cf. Tables 1 and 3). Higher concentrations were not tested as they were assumed to be irrelevant on the basis of what dilutions brackish shore communities would probably be exposed to (Simensen and Liseth 1967).

The observation of poor algal and animal communities on the shores of the outer Glåma estuary was tentatively explained as an effect of combined stress from variable salinity, particulate matter and the conspicuous rust brown cover on the substrate, extending about 5 km downstreams of the outfall (Knutzen et al. 1974, Bokn et al. 1976). Thus there are indications, but no conclusive evidence, for some damaging effects on shore organisms in this area.

Extensive studies of estuarine shallow water habitats have been conducted in the vicinity of the outfall from the Nordemham TiO_2 factory on the Weser. As mentioned above this discharge is of recidual acid (Wienecke 1982) with less acidity (pH 2-2.5) and considerably lower concentrations of iron (34-78 mg Fe/l) than the main waste dumped in the German Bight. Daily discharge has been 20-32000 m^3 (Wienecke op.cit.). On the basis of investigation before (1968) and after (1973) start of the production Michaelis (1973) reported markedly impaired fauna downstream of the discharge. The fauna was found to be practically eradicated close to the outfall and subnormal biomass was observed at a distance of about 1 km. Impact on the community structure was observed even farther off.

After these observations further surveys were made in the years 1975-1976 and 1979-1980. Statements about the negative effects from the acid iron waste are complicated due to the role of other waste and large natural variations from year to year, particularly with regard to biomass. No definite conclusions can be drawn about cause and effect, but there are some signs of a partly deteriorated environment in comparison with 1969 data:

- The crustacean *Neomysis integer*, otherwise very common in estuaries, has disappeared.
- Lower animal density (individuals/m^2) and biomass (weight/area) at the most waste affected localities (about 500 m downstreams of the effluent outfall).

There was no observable change in diversity of the rather poor animal communities (Wienecke, 1982).

From the Humber estuary Wilson and White (1974) reported a small abiotic area proximate to the outfall. The abiotic area was somewhat smaller than the about 0.35 km^2 deadly zone appearing from experiments with caged *Crangon crangon*. In this way periodically deadly waste concentrations were observed to extend ca. 1 km upstream and downstream of the discharge site. Outside the abiotic area some burying animals (nematodes and the polychaete *Nephtys* sp.) were the first to occur, thereafter species which live permanently above the sediment (shore crab and brown shrimp). The absence of mobile species like *Carcinus* in the most exposed area was explained as perhaps being the result of avoidance reactions, these being apparent below pH 6.0 in experiments with dilutions of different acids in seawater (Fig. 10 in Wilson and White, 1974).

As to other changes of biota in the effluent exposed area of the Humber estuary, reference studies prior to discharge are lacking. In the period 1959-1972 there has been a decline in abundance of the bivalve *Macoma baltica* at some of the monitoring stations, whereas the polychaet *Nereis diversicolor* showed increased abundance and other species had maintained their occurrence(Wilson and White, op. cit.).

Biotests with species of soft bottom habitats are rather sparse. Wilson and White (1974) reported reduced growth in the polychaete *Ophryotrocha* sp. and 96 hours LC_{50} of *Nephtys* sp. and *Macoma baltica* at dilutions exceeding 1:1000 .(Growth of *Ophryotrocha* was impaired by 1: 500, but was the same in 1:1000 as in the control culture). In comparison, Åkerson (1970) tested *Ophryotrocha labronica* in various concentrations of sulpuric acid and observed decline of growth at pH about 6.6. Considerably increased mortality was evident at pH below 6.0.

In the Finnish recipient area outside the Vuorikemia factory extensive damage to the soft bottom fauna has been reported from the extensive studies by Häkkilä et al. (1978). Other, less detailed accounts from this area, include the papers of Lehtonen (1975, 1976), Voipio and Niemistö (1975) and Isotalo and Häkkilä (1978).

Based on density and biomass of animals from nearly 100 sampling stations in the proximity and farther from the outfall, Häkkilä et al. (op.cit.) classified the neighbouring environment as a strongly polluted area of about 8 km^2 around the pipe outfall at 17 m depth, characterized by no or very sparse bottom fauna. Occasional animals could be found within 1-2 km, though. An additional area of about 18 km^2 was also markedly polluted. Here too, biomass, density and number of species were strongly reduced. This area extended up to 7 km from the outfall. "Semipolluted" soft bottom communities were recorded over an even larger area and were traceable at a distance of 10 km. According to previous observations the affected area has been slowly increasing between the years after start of TiO_2 production in 1961 and 1975-76. Possibly, some signs of improvement have accompanied reduced load of ferrous sulphate towards the end of that period (Häkkilä et al., op.cit.).

Other symptoms of pollution found by Häkkilä et al. (1978) were deviation in the size distribution of local *Macoma baltica* populations. Distinct disturbances of population parameters were observed as far as 10-15 km west of the outfall. Heavy cover of iron precipitate and corrosion of *Macoma* shells were abundant more than 10 km from the point of discharge (Figs. 23 and 24 in Häkkilä et al. 1978).

Table 5. Summary of results and experimental conditions (approximate pH and iron concentrations in mg/l) from tests with acid iron waste and bottom dwelling, shallow water organisms. (See text for further information. Note that the dilution figures refer to wastes of different composition, cf. Table 1.)

Test organisms	Increased mortality			Sublethal effects			References
	Waste dilution	pH	Iron conc.	Waste dilution	pH	Iron conc.	
Gammarus fasciatus	1:55[1]		10[1]				ERCO and ERCORESEARCH 1980
Gammarus sp.	1:350[1]	~ 4.6-5.6[2]	33[1]				Häkkilä 1978
Pontoporeia affinis	1:550[1]	~ 5.8-6.5[2]	20[1]				
Idotea baltica	1:440[1]	~ 5.5-6.4[2]	25[1]				
Macoma baltica	1:310[1]	~ 4.0-5.0[2]	37[1]				
Mytilus edulis	~ 1:500[1]	~ 6.4-6.7[1,3]	~ 25[1]				Wilson and White 1974
Aremicola marina	~ 1:350[1]	~ 6.2-6.5[1,3]	~ 30[1]				
Littorina littorea	~ 1:300[1]	~ 5.7-6.3[1,3]	~ 40[1]				
Carcinus maenas	~ 1:160	~ 3.8-5.5[1,3]	~ 75[1]				
Crangon crangon	~ 1:360[1,4]	~ 6.1[1,4]	~ 30[1,4]				
Ophryotrocha sp.				<1:500	<6.4-6.7	<25	
Crangon crangon	1:1000[5]		~ 45				Commission of the European Communities (1975)
Mytilus edulis	1:8000		~ 6				
Nereis diversicolor	1:2000		~ 25				

1) Calculated for this review
2) pH as measured at the start of test and after 96 hours (cf. Häkkilä 1978, Fig. 3 and Table 1)
3) Approximate start pH in experiments, estimated from Wilson and White's Fig. 1. Interval represents dilution in respectively estuarine and full sea water
4) Estimated from Fig. 4 in Wilson and White (1974), showing waste dilutions as observed in the recipient from pH and iron data
5) Montedison waste tested by CERBOM

From the dumping sites of the German Bight, New York Bight and off Delaware Bay (also on the east coast of USA) no or merely uncertain indications of damage to bottom fauna have been reported (EPA, Anonymous 1982c). As to results of investigations in the New York Bight, it is referred to Arnold and Royce (1950), Redfield and Walford (1951), Owen (1956, 1958), Vaccaro et al. (1972), Ketchum (1974) and to statement by U.S. Environmental Protection Agency concerning application for dumping permit from National Lead Industries Inc., Sayreville (Anon. 1982c). At the other U.S. dumping site, Lear et al. (1974) found that benthic community structure gave no indications of pollutional effects. However, they refer to earlier investigations at the same site with observations of "unexplained mortalities of sand dollars in proximity of acid waste dumpsite" (Lear et al., op.cit.).

Monitoring of the dumping site off Helgoland was based on reference investigations before starting of waste disposal in the area (Stripp and Gerlach, 1969). In spite of the many years gone rather few data are available from later surveys. After monthly grab sampling in the year follwing the start of dumping in March 1969, Rachor (1972) found som loose ferric hydroxide precipitate on the mucus of polychaete tubules and indications of elevated iron content in the guts of these animals. However, when compared to the results of Stripp and Gerlach (op.cit.) no significant change from numbers of individuals prior to dumping was observed. There were examples of recruitment and settlement of larvae in spite of flakes of ferric hydroxide floating just above the bottom. Lorenzen (1974) investigated the nematode fauna and confirmed that no adverse effects could be seen one year after dumping. Rachor and Dethlefsen (1974) referred to an unpublished thesis by Klein (1973), showing no disturbance of the population of a tube dwelling amphipod within the bottom area influenced by dumping. Referring to Rachor (1972) and unpublished results, they maintain that no deleterious effects on bottom fauna have been found in the period 1969-1974.

In the Hvaler archipelago of Norway indications of probable damage to soft bottom communities have been observed, notably by the lack of detritus feeding mussels (Knutzen et al.,1974, Bokn et al., 1976). The affected locality is situated about 2 km downstream of the outfall, the substrate of which was covered by a conspicuous, loose cover of iron precipitate, (several mm thick). Knutzen et al. also speculated that the absence of one otherwise abundant filter feeding mussel (*Mysella bidentata*) was caused by the precipitate clogging the feeding apparatus. This species was present at a station 6 km from the outfall, but the shells were heavily covered by iron flocs. It should be added that other filter feeding mussels were found at the most polluted locality. Recent and more detailed studies have confirmed that the acid iron waste has modified the surface of the substrate and affected the soft bottom community (B. Rygg, pers. comm.). Information about how far the effects are traceable must await final analysis of the material.

In the table summarizing the lowest waste concentrations which have proved to be effective in various studies (Table 5), some of the species seem to be surprisingly tolerant of low pH, particularly the mussel *Macoma baltica* and the shore crab. Unfortunately, results from test aiming at the observation of sublethal or chronic effects are limited to one study.

7.4 Fish

Bioassays have been performed with fish from both freshwater, brackish and marine habitats. As in the previous chapters on other groups of organisms a summary of the described test results has been given in tabulated form (Table 6).

Effects of the waste dumped in the German Bight (Table 1) were investigated by Kinne and Rosenthal (1967) and by Kinne and Schumann (1968). The former tested effects on fertilization, development of egg and larvae, and on behaviour of herring larvae (*Clupea harengus*). In dilution 1:16000 of aerated waste fertilization percentage decreased to the half of control value. It was also observed decrease in the diameter of eggs, increased egg mortality and augmented fetus heart beat frequency. Hatching was accelerated, concomitant with reduced hatching percentage. Further, growth of larvae was slower and the majority of them were malshaped. In experiments with fertilized eggs, increased lethality was observed only in dilution 1:8000, but abnormal heart beat rhythm and one day advance of hatching occurred in dilutions up to 1:32000 (Kinne and Rosenthal, 1967). In all dilutions eggs were covered by a brown precipitate.

In the same author's experiments with 1-3 days old, and previously unaffected larvae, it was observed that merely 1 hour in dilution 1:8000 resulted in increased mortality in the following days. No significant increase of death rate was observed in dilution 1:16000-1:32000, but behaviour was markedly affected (swimming in spirals in dilution 1:16000 and failure of prey seeking movements in 1:32000).

Conditions of pH during tests have not been given by Kinne and Rosenthal. It may be inferred, however, from information given by Kayser

(1969) and by Kinne and Schumann (1968, addendum), that pH of the above mentioned dilutions have not been much below 7.0-7.5, even in the least diluted test medium. In any case, as media were aerated and either not changed or changed just once during the test period, exposure to the least favourable pH was of short duration.

30 hours assay with the same waste and the bottom living flatfish *Solea solea* resulted in (not statistically significant) increased death rate of 6 days old larvae in dilutions up to 1:20000 (Kinne and Schumann, 1968). 24 h LC_{50} was 1:15000. Younglings of *Gobius pictus* appeared to be more tolerant with respect to acute effects; 24 h LC_{50} estimated to be about dilution 1:6000 (Kinne and Schumann, op.cit.). Elder fish were even less sensitive. Not statistically significant increase of mortality was observed in dilution 1:12000 - 1:32000. Increased frequence of gill operculum movement was observed in dilutions up to 1:32000. This effect was more pronounced in fresh compared to aged medium. The significance of this factor was confirmed in experiments with 3 weeks old larvae of *Agonus cataphractus*; 100 % mortality occurring at dilutions 1:5000 and 1:15000, respectively with 24 hours and 4 hours old waste mixture. Some conclusions with regard to the pH conditions in the experiments of Kinne and Schumann (1968) can be inferred from an addendum to their paper. These tentative conclusions are given i Table 6. It is seen that pH probably has not been below 6.5 and in all higher dilutions above 7.0. This may imply that other factors than acidity and/or increased CO_2 partial pressure have been the causative agents behind the observed harmful effects.

Halsband (1968) tested the effects of probably less concentrated waste (cf. chapter 7.3) upon rainbow trout (*Salmo gairdneri*) and other fish species: *Gasterosteus aculeatus, Pleuronectes platessa, Agonus cataphractus* and *Zoarces viviparus*. Results are only given for *Salmo gairdneri* with regard to oxygen consumption and other physiological and biochemical variables. Halsband conludes that the tolerance limit was below waste dilution 1:40. If the previous assumptions about waste source and composition are correct, this dilution corresponds to about 1-2 mg Fe/l.

According to ERCO (1982) several fish tests have been performed with waste from NL Industries and Du Pont. Unfortunately, reports of these studies have not been accessible in connection with the present review. The lowest environmentally protective concentrations (EPC, cf. chapter 7.1) as quoted by ERCO (1982) were 20 ppm (96 h) of NL waste (ERCO, 1978, 1981, 10 % application factor from mortality studies) and < 12,5 ppm (4800 h) of Du Pont waste (Falk and Philips, 1977), corresponding to about 0.7 mg Fe/l and < 0.5 mg Fe/l, respectively. It should be stressed that in accordance with the definition of EPC the quoted figures are supposed to be safe (no effect) levels.

The effects of waste from the two Canadian producers discharging to the St. Lawrence River (Table 1) were tested in bioassays with various life stages of the rainbow trout (ERCO and ECO-RESEARCH, 1980). In static tests 96 hours LC_{50} for juveniles were determined to dilution about 1:70 and ca. 1:600, respectively for the Varennes and Tracy wastes. (In flow-through tests with Tracy waste the 96 h LC_{50} was somewhat unexpectedly determined to a lower dilution than in the static test: ca. 1:250. However, both acidity and ferrous iron concentrations appear to have been somewhat higher in the flow-through assays.) The bluegill (*Lepomis macrochirus*) showed similar tolerance of Varennes waste as rainbow trout. In long term tests with Tracy waste, deviations from control results respecting survival and hatching of trout eggs and survival of larvae were observed in dilution ca. 1:1100, whereas 1:5000 showed no adverse effects. Maximum allowable toxicant concentration was determined as 1:2400, i.e. about 0.5 mg Fe/l.

With regard to the effluent from the Finnish factory Lehtonen (1975) refers to the results of Seppänen and Shemeika (1972) who observed increased lethality in dilution > 1:200 in 96 hours tests with perch (*Perca fluviatilis*) and whitefish (*Coregonus lavaretus*), and sublethal responses at dilution 1:500.

Häkkilä (1978) found that the 48 hours median tolerance limits were about dilution 1:300 for *Phoxinus phoxinus* and *Pungitius pungitius*. For the minnow (*Phoxinus phoxinus*) 7 days TL_m decreased to 1:400.

According to the information about development of pH in media with the above waste dilution, this means rather high tolerance of low pH levels (cf. Table 6). Separate tests in solutions of sulphuric acid and ferrous sulphate showed that the median tolerance limits of minnows were pH 4.4 (96 h) and about 250 mg Fe/l (48 h, pH $\sim$ 5.3). These results pointed to low pH as the main toxic factor. (The apparent high tolerance of acidic conditions may perhaps illustrate the difficulty in applying conclusions from laboratory results on populations or communities. In nature minnows are hardly found in habitats with pH below 5.5 (Almer et al. 1974).

In avoidance reaction tests with minnows in aerated waste, ferrous sulphate and sulphuric acid Häkkilä (1978) observed some response in a waste dilution corresponding to 0.36 mg Fe/l (pH 7.6). The same iron concentration was effective when the test was performed with ferrous sulphate. Interpretation of these results is complicated, however, by the lack of consistent increase in the strength of response with higher iron concentrations. Further, pH 7.0 caused as strong avoidance reaction as 0.36 mg Fe/l. pH 6.0, belonging to the natural pH range met by minnows, provoked nearly the same response as 1.2 mg Fe/l and 3.6 mg Fe/l, respectively in solutions of ferrous sulphate and waste water.

Behavioural, physiological and biochemical response variables have been used in a series of fish tests by Lehtinen and co-workers to evaluate the potential hazards from the Vuorikemian effluent. Lehtinen (1980) tested the ability of perch (*Perca fluviatilis*) and bleak (*Alburnus alburnus*) to withstand water rotation in waste dilutions in the range about 1:3300 - 1:1650. Both species showed decreased capacity in this respect, even in the highest dilution. (Statistically significant deviation from control only in the least diluted medium for bleak.) The result is attributed to the brown precipitate on the gill surface, possibly by mechanically impeding respiration or by toxic constituents of the precipitate. In this connection it deserves mentioning that analysis of the tested waste showed higher concentrations of cadmium (0.12 mg/l) and copper (1.5 mg/l) than stated in Table 1. (Concentrations of zinc and lead were somewhat lower.) Information about pH conditions is not given, but should not be of importance in so high dilutions (cf. Häkkilä, 1978).

In subsequent studies Larson et al. (1980) looked at biochemical and hematological effects in flounder (*Platichtys flesus*). After fourteen days several typical stress responses were observed in fish exposed to the lowest dilution (about 1:2700): disturbed ion balance (indicative of impaired osmoregulation ability), elevated concentrations of glucose and lactate in the blood, and increased hematocrit, hemoglobin content and number of erythroblasts, and, finally, a reduction in the spleen somatic index and in the number of lymphocytes. Most of the deviations were statistically significant.

In a recent paper Lehtinen and Klingstedt (1983) reported on the investigation by x-ray analysis in the scanning electron microscope of the brown gill precipitate of perch exposed to waste dilutions 1:3300 - 1:1650 for 28 days. In this deposit they found high levels not only of iron and titanium but also of phosphorous, potassium and calcium, probably as a result of co-precipitation. The consequenses of these findings are discussed with respect to several mechanisms which may serve to enhance metal toxicity as a result of change in the microclimate of the gill epithelium.

With the British Titan Products effluent Wilson and White (1974) observed markedly depressed rate of heart beats of *Agonus cataphractus* in dilution 1:1000.

In fish tests conducted by CERBOM with Montedison waste, as referred to in a Commission of the European Communities report (1975), toxic effects to the most sensitive fish species were found with a dilution as high as 1:35000 when the fishes were held in the waste for 10 days. The toxicity threshold for *Labrus berggylta* was reported to be 1:16000, whereas dilution 1:1000 was lehtal to the eel (*Anguilla anguilla*) and to sand goby (*Pomatoschistus minutus*) within 48 hours.

From their fish tests with the Italian and French effluents Maggi and Lassus (1974) reported no increased mortality in the dilutions 1:2000 of the Montedison waste, and in 1:500 of the Thann et Mulhouse and Tioxide wastes. The doubled concentrations were all acutely lethal, presumably from the very depressed pH levels (2.8-3.3).

Table 6. Summary of results and experimental conditions (approximate pH conditions and iron concentrations in mg/l) from tests with acid iron waste and fish. (See text for further information. Note that the dilution figures refer to waste of different composition, cf. Table 1.)

Species	Increased mortality			Sublethal effects			References
	Waste dilution	pH	Iron conc.	Waste dilution	pH	Iron conc.	
Clupea harengus	1:8000	~ 7.0-8.0	12	1:32000		3	Kinne and Rosenthal (1967)
Solea solea Gobius pictus Agonus cataphractus	1:15000 1) 1:6000 1) 1:15000 2)	~ 7.3-8.0 3) ~ 6.5-7.0 3)	7 17 17	1:32000	7.4-8.0 3)	3	Kinne and Schumann (1968)
Salmo gairdneri Lepomis macrochirus Salmo gairdneri	1:70 4) 1:70 4) 1:600 5)	< 6.2-6.9 6) < 6.2-6.6 No data	8 8 2	1:1100		1.1	ERCO ans ERCO-RESEARCH 1980
Phoxinus phoxinus Pungitius pungitius	1:400 7) 1:300 7)	5.4-6.0 8) 3.7-4.3-5.0 8)	30 40				Häkkilä 1978
Alburnus alburnus Perca fluviatilis				1:3300 1:3300		3.6 3.6	Lehtinen 1980
Platichtys flesus				1:2700	7.2 ± 0.2	4.4	Larson et al. 1980
Agonus cataphractus				1:1000	~ 7.0 9)	8	Wilson and White 1974
Pomato schistus minutus Anguilla anguilla Labrus berggylta	1:1000 1:1000		~ 40-50 10) ~ 40-50	1:16000		~ 4	Commission of the European Communities (1975)

1) Not statistically significant increased death rate in dilutions 1:20000
2) 4 hours old waste, 1:5000 in 24 hours old waste
3) Development in the course of 24 hours in non-aerated medium, cfr. appendix to Kinne and Schumann (1968)
4) Approximate 96 h LC_{50} with Varennes waste
5) Approximate 96 h LC_{50} with Tracy waste
6) The quoted figures show development of pH 0-96 hours in dilution 1:100
7) 48 hours (Pungitus), respectively 168 hours (Phoxinus) median tolerance limit
8) Development of pH in test media at times 0.24h, 72h
9) Incipient pH according to Fig. 1 in Wilson and White (1974)
10) Assuming about the same iron concentration as in Table 1

Undisputable damage to fish population and fisheries has been demonstrated in the Finnish recipient area (Voipio and Niemistö, 1975; Lehtonen 1975, 1976; Häkkilä 1978, Häkkilä et al., 1978, Järvinen, 1982). Lehtonen (1975, 1976) reported that in field experiments, eggs of the pike (*Esox lucius*) were covered by a brown deposit up to 3.5 km from the outfall. They hatched as close as 1 km, though. He also reported that fish died in cage nets 5 km west of the pipe outfall. Even at a distance of 13 km dead fish in nets have been observed with typical symptoms, as if they had been boiled. Fish catch of the area has decreased since the early 1960's to about 1/3-1/2 (Lehtonen 1976), partly due to ectra work to wash iron deposit off nets and traps. Only a few km^2 are permanently devoid of fish, but occasional absence occurs over an area of about 25 km^2.

The most dramatic account of harm to fish has recently come from Järvinen (1982). According to this paper, starved baltic herring with blood red eyes, or fish even without eyes, have been observed along a considerable stretch of the coast in the neighbourhood of the Vuorikemian recipient area. Iron accumulation has been demonstrated in the spleen of the sick fish, and there are signs of a steadily decreasing herring population.

Reports of damage to fish in the Norwegian recipient area have been limited to death of eel in traps situated less than 2-300 m from the outfall. In other waste receiving areas the question of hazard to fish has been hotly discussed for decades. Summing up experiences from the previous NL Industries dumping grounds EPA (Anon. 1982c) concluded that "significant adverse impacts to fisheries have not been demonstrated". Some of the basis for this conclusions have been provided by Westman who have reported his own investigations and summarized other observations in several reports (Westman 1958, 1967, 1969). The latter two papers have not been available for this review. Other evidence in the same direction has come from the studies by the National Oceanographic and Aeronauties Administration (Swanson, 1977, not available for this review). The above conclusion was reached in spite of several testimonies from professional and amateur fishermen to the effect that harm to fisheries has occurred (partly referred to by EPA, Anon. 1982c).

Longwell and Hughes (1980) observed significantly lower mackerel egg viability in New York Bight areas influenced by acid iron waste and other contaminants. As no causal relationships have been established it remains a mere speculation that acid waste should be one of the contributing factors. Longwell and Hughes (op.cit.) seem rather to emphasize the role of hydrocarbons and metals in general.

With regard to impact on fish populations at the European dumping sites, for several years no negative effects were claimed (Dethlefsen, 1973, Rachor and Dethlefsen, 1974, see also de Clerk and van de Velde

(1974)and report of the Commission of the European Communities (1975)). However, more recent large-scale investigations of fish diseases have revealed and apparent link between frequency of certain ailments and waters influenced by the acid waste. This associations have been indicated for lymphocystis (a virus disease) and epidermal papillomas (wartlike tumors of the skin) in the North Sea dab (Dethlefsen 1978, 1980). Several other species and types of disease were also observed, without finding any abnormal disease frequency on fish from the dumping site (Dethlefsen 1980).

Inspection of more than 100000 dabs from seven cruises in 1977-1980 still showed an above average frequency of epidermal papillomas on dab from the waste influenced area, but were no longer claimed for lymphocystis (Dethlefsen and Watermann, 1980). The authors did not find any correlation between condition factor (general fitness) of the fish and occurence of the epidermal disease. Both Dethlefsen (1980) and Dethlefsen and Watermann (1980) are cautious in their conclusions with regard to a causal relationship, but maintain that there are clear indications that the waste and disease are connected.

Based on similar data from inspection of fish disease frequency in the German Bight Möller (1981) disputes this connection. He claims to have found a statistically significant correlation between both diseases in question and the condition factor of the fish (Möller 1978, 1981). He also calls attention to observations of a higher frequency of epidermal papillomas in dab of increasing length. If this factor is considered, the higher frequency of the disease on dab from the waste site, as observed by Dethlefsen and Waterman, is not statistically significant (Möller 1981). That epidermal papillomas were more abundant in dabs above a certain length had already been observed by Dethlefsen.

From the report of a recent meeting in the Standing Advisory Committee on Scientific Aspects of the Paris and Oslo Commissions (Anon. 1982d) it appears that the Federal Republic of Germany has continued large-scale epidemiological investigations of fish disease in the German Bight and the North Sea. The project period is 1981-83, and the studies also comprise Dutch dumping areas for acid waste.

8. DISCUSSION AND CONCLUSIONS

Acid iron waste has a complex nature. Even more complicated are the physical and chemical reactions which take place in recipient. Several mechanisms of toxicity and physical stress are possible and interwoven. To evaluate these in detail is a difficult task beyond the scope of this review, the main aim of which is to collate the available information and to draw some conclusion emanating from this knowledge (or lack of it). To meet this purpose in a concise way it has been found appropriate to simplify the problem by treating the main factors separately.

8.1 Effects from acidification

Decreased pH can act toxic in its own power or by the concomitant increase of carbon dioxide partial pressure. With respect to the latter it is fundamental for the internal (cellular) environment of both animals and plants due to its role in respiration and photosynthesis. Hence the capacity to regulate the internal CO_2-environment will be important for the tolerance of external change. This leads to the speculation that unicellular and other small organisms generally will be most sensitive.

Elevated external carbon dioxide level makes outward diffusion of the CO_2 formed in respiration more difficult. Further, increased CO_2 concentration acts on the respiratory pigments, often to the effect that the oxygen affinity increases. High CO_2 concentration also stimulates the respiratory activity of animals. Usually this has a beneficial effect due to accompanying undersaturation of oxygen.

Several authors have demonstrated that the normal carbon dioxide pressure in seawater is below the photosynthesis saturation level (Paasche 1964, Ogata and Matsui, 1965, Simpson et al., 1978). Theoretically, then, slight acidification might stimulate primary production. Also it should be pointed out that the risk of effects from increased CO_2 partial pressure in the main is restricted to salt water or freshwater localities with high alkalinity; soft freshwater having too low carbonate content.

Marine recipients

The actual tolerance and reaction of marine organisms to increased carbon dioxide pressure has attracted modest attention. One of the reasons may be experimental difficulties (separations of pH from carbon dioxide effects, control and recording of the experimental conditions).

From an addendum to the paper by Kinne and Schumann (1968) it appears that under unaerated conditions in the laboratory the theoretical partial pressure of carbon dioxide is elevated several times for many hours, even in dilution 1:32000. In the areated culture medium pH rose above 8.0 in the course of 2-3 hours by stripping of CO_2 from the water. The actual recipient conditions will depend on turbulence and aeration of the polluted waters. Consequently, discharge to calm surface water (or into deeper water) would be relatively more hazardous.

Reviewing the effects of acidification in the marine environment Knutzen (1981) concluded that there was little evidence of harm caused by decrease of 0.5-1.0 pH units. From the tables summarizing treshold toxicity concentrations of the waste (Tables 3-6) it is seen that in several cases effects have been demonstrated when pH was above 7.0. However, separate effects from pH above this level have not been observed. In any case, studies at the dumping sites have demonstrated that pH below 7.0 is of short duration and that approximately normal pH is restored within 1-2 hours (cf. chapter 5.1).

It may be concluded that damage caused by acidification in itself most probably will be of little significance at marine dumping sites in open waters.

The situation in estuaries and coastal brackish waters is somewhat different. The observations in the Bothnian Bay and the rivers Humber and Glåma make it obvious that adverse pH levels (below 7.0) are more or less permanent in part of the water volume; in the Humber shifting with tides and in the Bothnian Bay with direction of wind and currents. Acidity affected areas would in all probability be limited to a maximum of

1-2 km (Humber and Glåma) or 4-5 km (Bothnian Bay) from the outfalls. Particularly the situation in the Pori area shows that negative effects from acidification are to be expected when it is difficult to obtain rapid dilutions.

Freshwater localities

Freshwater species are adapted to lower pH than marine organisms and community structure are rarely changed before pH goes below 6.5. In the only freshwater recipient considered here, the St. Lawrence river of Canada, pH below 7.0 was not observed at distances above 300 m from the outfall, and then limited to relatively small water volumes along one side of the river. Hence damage from acidification is not probable.

8.2 Effects from metals

As a first basis for evaluation it might be of some use to compare waste concentrations with water quality criteria. Table 7 gives a summary of this information. As waste concentrations there are used worst case data - i.e. the highest concentrations mentioned in Table 1 for each of the selected metals. The purpose of this simplified approach is not to state which recipient concentrations may be regarded as safe or acceptable, merely to give an idea of which waste constituent may represent the greatest problem.

The freshwater and seawater criteria have been quoted or rounded off from EPA (1976, mostly revision of 1980). The 1980 guidelines for freshwater have been given as several concentrations depending on water hardness ($CaCO_3$ concentration) and length of exposure (series 1 and series 2 in Table 7). As to hardness dependence, the strictest criteria have been used. In saltwater only the limits of 24 hours average concentrations are listed. As no criterium for iron concentration in the marine environment has been given the freshwater criterium is used. All criteria refer to the total content.

For some of the waste constituents criteria are lacking, the most important of these being titanium and vanadium. The reason for lack of guidelines with respect to titanium probably is that this element is regarded as little toxic. In a report from the Commission of the European Communities (1975) it is claimed that with the exception of halides the salts of titanium are practically insoluble in water, and further, that titanium dioxide as constituent of medicine often is given in daily doses of more than 10 grams. As regards vanadium, little is known about its toxicities to aquatic organisms, but is not ranked among the dangerour metals.

Table 7. Worst case concentration of metals in acid waste compared to EPA water quality criteria to protect aquatic life (EPA, 1980; if not revised: EPA, 1976). Some of the criteria have been rounded off.

Component	Waste conc. salt water mg/l	Waste conc. fresh water mg/l	Salt water criteria (limit 24 h average) mg/l	Fresh water criteria 1 (limit 24 h average) mg/l	Fresh water criteria 2 (not to be exceeded)	Ca dilution to meet criteria		
						Salt water	Fresh water 1	Fresh water 2
Fe 1)	$100 \cdot 10^3$	$1.3 \cdot 10^3$	1 1)	1 1)		1:100000	1:1300	
Ti	$5.5 \cdot 10^3$	230						
Mn 1)	$1.3 \cdot 10^3$		10^{-1} 3)	$5 \cdot 10^{-2}$ 6)		1:13000		
V	$5 \cdot 10^2$	60						
Al	$14 \cdot 10^3$							
Cr 2)	$2 \cdot 10^2$	< 20	~ 10 4)	$\sim 4 \cdot 10^{-2}$ 7)	2.2	1:200	1:500	1:10
Zn 2)	75	60	$6 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	0.2	1:1300	1:1200	1:300
Pb 2)	12	< 0.3	$25 \cdot 10^{-3}$ 5)	$7.5 \cdot 10^{-4}$	$7.5 \cdot 10^{-2}$	1:500	1:400	1:4
Co	11							
Ni 2)	11	2.5	$7 \cdot 10^{-3}$	$56 \cdot 10^{-3}$	1.1	1:1600	1:500	1:2
Cu 2)	5	< 0.2	$4 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$12 \cdot 10^{-3}$	1:1300	1:40	1:20
Cd 2)	0.8	< 0.1	$\sim 4 \cdot 10^{-3}$	$12 \cdot 10^{-6}$	$1.5 \cdot 10^{-3}$	1:200	1:8400	1:70
Hg 2)	$3\ 10^{-2}$	$< 5 \cdot 10^{-3}$	$25 \cdot 10^{-6}$	$6 \cdot 10^{-7}$	$2 \cdot 10^{-6}$	1:1200	1:8300	1:2500

1) EPA (1976). Freshwater criterium used for iron in salt water
2) EPA (1980)
3) Criterium to protect consumers of shellfish
4) Inadequate data respecting chronic toxicity in sensitive species
5) Chronic toxicity
6) Criterium for water supply
7) Assumed toxicity threshold for trivalent chromium

With reserve for lack of criteria for some of the metals, for the disputable relevance of the guidelines, and, particularly, for the reliability of waste analysis data, it is seen from Table 7 that in salt water it appears that iron, followed by manganese, are the critical elements.

As regards iron, it is of some interest to note that a criterium of 1 mg/l corresponds to the lower limit of adverse waste concentrations observed in tests (ch. 7, Tables 3-6). One should also take heed of the fact that dilution 1:100000 will be characteristic of large volumes of water for several hours after dumping (for instance, minimum 1:67000 after 4 hours according to ERCO (1978) and 1:1000000 after about 11 hours according to Weichart (1977)). On the other hand, $100 \cdot 10^3$ mg Fe/l is a maximum figure, and evaluation of the real risks should be based on in situ data from the individual dumping sites. In any case, most major dumping sites at sea receive waste with iron content above or close to 50 g/l, hence the dilution required to reach an ambient level of 1 mg Fe/l is about 1:50000 - 1:100000.

With regard to the other potentially critical elements in the marine environment, it is obvious that any assessment is heavily dependent upon the reliability of results from waste analysis. If for instance the next highest concentration given for manganese in Table 1 is considered, the necessary dilutions to "meet the criterium" would be 1:6000 in stead of 1:13000. 1:6000 is a dilution reached in dumping areas within less than one hour after barging. For all other metals "the guidelines will be met" - except in isolated packets of water - in about 15 minutes after dumping.

For the effluents discharged to the rivers Glåma and Humber there are particularly inadequate analysis data for theoretical assessments, except as regards iron. The required dilutions to reach 1 mg Fe/l would be about 1:3000 and 1:8000, respectively. In the Glåma estuary dilution of this order is to be expected at distances about 3-4 km from the outfall (in that part of the brackish water flow which is affected by the waste). Within the waste plume, concentrations above 1 mg Fe/l are to be expected even farther from the outfall in the Humber, owing to less effective initial dilution.

Provided that the waste composition is correct (which is questionable) calculations indicate that the other metals in the Kronos Titan effluent discharged into Glåma require maximum dilutions of 1:200 (manganese) or less than 1:100.

The Vuorikemia case is difficult to assess in this way, due to the low salinity (5-6 o/oo S) of the water and because direct information about waste dilution is lacking. From what has been described about conditions in the recipient area, it is nevertheless probable that the 1 mg Fe/l limit is exceeded from time to time several kilometers (5-10 ?) from the outfall.

In the St. Lawrence river, the critical metals probably are cadmium and mercury, followed by iron. (Some reserve must be taken for lack of manganese data.) Dilutions less than 1:8500 will occur in waste affected packets of water many kilometers downstream of the outfall to the St. Lawrence river, but only in water volumes which are small compared to total river flow.

8.3 Effects from iron hydroxide flocs

It has been established that the precipitation of ferric iron hydroxide causes increased turbidity and thus impairs amenities. The latter effect is of minor importance except in estuaries and coastal areas. Often the effect will be somewhat masked by high natural turbidity. The deposit on shores in the Hvaler archipelago is an example of unwanted consequences.

As regards phytoplankton and zooplankton, there are no field observations indicating significantly negative effects. Keeping in mind the results from biotests, particularly those of Kayser (1969), it is obvious that potentially harmful concentrations may occur for some hours after barging and in waters far from land based contamination sources. Unfortunately, the biotests with plankton organisms have not given any clue to distinguish among causal factors. Therefore it is not possible to assess the role of flocs as such, for instance in the feeding of zooplankton.

Probably more important are the adverse effects of iron flocs on shore communities, bottom fauna and fish living in the vicinity of estuarine or other coastal outfalls. The negative effects observed in the Humber estuary, the Hvaler archipelago and especially in the Bothnian Bay are all linked with iron deposits in the observed habitats. Several mechanisms are active: smothering of substrate, clogging of respiration and feeding apparatus, interference with absorbtion of food from the intestine and release of toxic metals in the microenvironment of the organisms. The latter mechanism has been maintained by Larson et al. (1980) and Lehtinen and Klingstedt (1983) to be important in fish having the flocs deposited on their gills. The field observations in the Pori recipient area (and Winter's *Mytilus* studies) strongly indicate that long-term studies of sublethal effects would show effective concentrations below the values listed in Table 5.

One of the possible speculations in this connection is about the role of chromium, manganese and aluminium, which probably are important constituents of the flocs due to co-precipitation. May for instance the trivalent chromium be oxidized to the more toxic hexavalent state? Such a reaction is known to occur in the presence of manganese oxide (Jenkins, 1982).

In conclusion, it seems to be little doubt about the negative effects from ferric hydroxide flocs with associated metals. The extent of effective concentrations, stated in water volumes and distances from various sources, are difficult to assess, though. The main reasons for this are the effects caused by other properties of the waste and inadequate data from field as well as laboratory studies.

8.4 Impact from oxygen demand

Perhaps with the exception of the affected part of the Bothnian Bay, and to a lesser extent the soft bottoms of the Glåma estuary, it is not plausible that decreased oxygen tension plays any significant role (cf. chapter 4). Probably it is a minor factor even in the above recipients. Exceptions to this may be small depressions of the bottom in the close proximity of the outfalls, characterized by inadequate water renewal.

8.5 Accumulation of waste constituents in biota

With certainty, such accumulation has merely been demonstrated for main components of the waste. On the other hand, this problem should be subject to further studies in the vicinity of pipeline outfalls. Accumulation in organisms from dumping sites is far less probable and has not been demonstrated beyond doubt. Biomagnification has not been observed, neither is it probable with regard to the main constituents (iron, manganese, titanium, chromium, vanadium). Hygienic consequences are not possible to evaluate as guidelines respecting concentrations of the above metals in seafood are not used).

8.6 Further research

The purpose of this section is not to argue that more research is needed before management decisions are made. The pollutional state of the described estuaries and in the Bothnian Bay is reasonably well established. Consequently, there are more or less adequate basis for decisions.

On the other hand, the consequences of dumping in the open sea are still a matter of speculation. To some extent experimental evidence is in disagreement with field observations. Further, it should be emphasized that the scientific understanding of the problem is far from satisfactory. (This statement also applies to the impact in estuaries and particularly in those parts of the coastal water habitats of the Bothnian Bay and the Hvaler archipelago in which effects are suspected, but not clearly demonstrated.)

Firstly, the relative role of the acid versus the other components have attracted some attention but far from enough to give full understanding of the problem. To this purpose it is recommended long-term and life cycle experiments to study sublethal effects in a broad spectre of organisms. Parallel tests should be conducted with the waste and pure acid and one should be aware of the influence on results from aging of the waste and aeration or not of the media. One of the main aims of such experiments should be to describe not only the development of pH but also of carbon dioxide partial pressure with time.

In this connection it deserves mentioning that we are in general need of better understanding of the possible consequences from acidification of seawater (Knutzen, 1981). Under certain circumstances this may be a coming environmental problem caused by sea water scrubbing of stack gases from coal and oil fired power plants (Bjerkeng and Knutzen, 1982).

It is also a need of long-term tests on the sublethal effects of the ferric hydroxide flocs of the waste. If possible, release of dissolved metals from the flocs should be focused on within the scope of the bio-assays, as a means of describing the experimental conditions. To evaluate the possible consequences at dumping sites it would be of particular interest to study effects on zooplankton (including fish larvae) and soft bottom fauna. In coastal areas,the effects on benthic primary producers are in need of elucidation.

To evaluate the environmental implications of results observed in laboratory experiments with iron flocs, it is necessary with better data respecting the quantitative distribution of iron at dumping sites. The course of waste dilution after the first 1-2 hours (dilution 1:20000 - 1:100000) is of particular interest.

Biological studies at the dumping sites should primarily aim at the effects on zooplankton (including fish larvae) and soft bottom fauna. In coastal areas high priority should be given to the study of effects on benthic algae.

Finally, it should be worth considering at least to supplement (or even partially to replace) large scale epidemiological fish surveys with long-term experiments in the laboratory.

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The following recent publication has not been included in the present review: Rückstände aus der Titandioxid-Produktion. Stand: Dezember 1981. Published by Umweltbundesamt, FRG. Berlin 1982. 221 pp.

The above report contains updated information on amount and composition of waste from factories in Western Europe and it also refers results of effect studies in Europe and USA. The informations about effects is the same as covered by this review and does not change the conclusions. However, some additional references may be of interest:

Becker, G.; Gienapp, H.; Schmidt, D.; Strübing, K.; Doerffer, R.: Flugzeugmessprogram in der Deutschen Bucht. - Umschau 79 (1979) S. 774 - 777.

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Offhaus, E. (Hrsg.): Abfallbeseitigung auf See. - Beihefte zu Müll und Abfall, H. 17, Erich Schmidt Verlag, Berlin 1980, 105 Seiten,

including the following contributions by Weichart and Dethlefsen:

Weichart, G.: Auswirkungen der Einbringung von Abfällen aus meereschemischer Sicht. - in Lit. 50, S. 79 - 80.

Dethlefsen, V.: Auswirkungen der Abfallbeseitigung auf See aus meeresbiologisher Sicht (II). - in Lit. 50, S. 87 - 90.

Rühl, N.-P.; Weichart, G.; Albrecht, H.: Chemische und sedimentologische Undersuchungen in der Deutschen Bucht im Zusammenhang mit der Einbringung von Abwässern aus der Titandioxid-Produktion. - in Salze und saltzhaltige Lösungen. Umweltbundesamt Materialien 2/78, S. 88 - 90. Erich Schmidt Verlag, Berlin 1978.

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