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International Council for
the Exploration of the Sea

C.M. 1977/C:3
Hydrography Committee
Ref. Fisheries Improvement Cttee
Plancton Committee



The pH in the waters of the German Bight as influenced by
primary production and respiration and by acid TiO_2 wastes

by

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Résumé

La valeur du pH dans l'eau de la Baie allemande dépend surtout de la production primaire et de la respiration. En hiver, c'est la dégradation de matériel organique qui est prédominante; la valeur du pH se situe entre 8,0 et 8,2. Pendant le printemps et l'été, la production primaire importante provoque, par endroits, l'accroissement de la valeur du pH dans la couche euphotique jusqu'à 8,50. Les eaux résiduelles très acides provenant de la production de TiO_2 ne provoquent qu'un faible décroissement de la valeur du pH dans la région des déversements et dans son voisinage. C'était seulement dans l'eau fraîche du sillage des bâtiments citernes de déchets qu'un décroissement important de la valeur du pH jusqu'à environ 4,0 a été constaté. Un accroissement continu de la concentration d'acides n'a pu être constaté dans la Baie allemande.

Zusammenfassung

Der pH-Wert im Wasser der Deutschen Bucht wird vor allem von Primärproduktion und Atmung beherrscht. Im Winter überwiegt der Abbau von organischem Material, der pH-Wert liegt zwischen 8,0 und 8,2. Während des Frühjahrs und Sommers bewirkt die starke Primärproduktion stellenweise einen Anstieg des pH-Wertes in der euphotischen Schicht bis auf 8,50. Die stark sauren Abwässer aus der TiO_2 -Produktion haben nur eine geringe Abnahme des pH-Wertes im Einbringungsgebiet und in dessen näherer Umgebung zur Folge. Lediglich im frischen Schraubenwasser der Abwasser-Tanker wurde eine starke Erniedrigung des pH-Wertes auf etwa 4,0 gefunden. Eine ständige Zunahme der Säurekonzentration in der Deutschen Bucht konnte nicht festgestellt werden.

Abstract

The pH-value in the waters of the German Bight is controlled, above all, by primary production and respiration. In winter, the decomposition of organic material predominates, the pH-value lies between 8.00 and 8.20. During spring and summer, the more intensive phytoplankton primary production causes a sporadic rise of the pH-value in the euphotic layer of up to 8.50. The strongly acid waste waters from TiO_2 production cause only a slight decrease of the pH-value in the dumping area and in its close vicinity. Merely an intensive reduction of the pH-value of down to 4.0 was found in the fresh screw-water of the waste water tanker. A continuous increase of the acid concentration in the German Bight could not be ascertained.

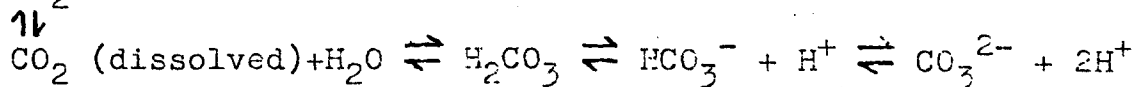
Introduction

Definition of pH:

$\text{pH} = -\log_{10} \text{H}^+$ ion activity.

Formulation of CO_2 system:

CO_2 (gas)



The CO_2 system of the sea is subjected to constant changes. Some of the reasons for that are: warming up or cooling down of the water; sinking down or upwelling (change in pressure); CO_2 exchange between seawater and atmosphere; **dissolution or precipitation of CaCO_3** ; supply of acids and bases from the sea bottom and the mainland into the seawater (volcanic eruption,

weathering, etc.). The most intensive changes in the CO_2 system are caused by organisms: In the primary production of plants, CO_2 is taken from the seawater and is fixed in the form of organic compounds (e.g. sugar, protein, fats, etc.); the pH increases. In the process of respiration organic compounds are broken down. The CO_2 which results thereby, is given off into the seawater; the pH decreases. Man also contributes to an increasing degree to the changes in the CO_2 system in the sea: for example, by the burning of coal, crude oil, and natural gas, or by the direct introduction of acids and alkalies into the seawater.

The pH-value is an especially important dimension for the calculation of the CO_2 system in seawater. To date, only relatively few pH measurements are available from the German Bight. In the Helgoland roads, during the winter, pH-values were found between 8.0 and 8.1. In summer, the decade mean value rose at times to 8.42 (Biologische Anstalt Helgoland, 1970 to 1973).

The introduction (dumping) into the German Bight of waste waters from titanium dioxide production which contained H_2SO_4 , was the reason for our investigations. The dumping area is about 20 to 30 km northwestwards of Helgoland. The water depth is 25 to 29 m. Since May, 1969, about 1300 to 1800 t daily of waste waters from titanium dioxide production have been dumped there. The chemical composition of the waste waters, according to the information provided by the Titangesellschaft mbH, Nordenham, is: about 14 % FeSO_4 ; about 10 % H_2SO_4 ; about 1.4 %

TiOSO_4 ; about 1 % MgSO_4 ; about 0.07 % MnSO_4 ; about 0.045 % VOSO_4 ; about 0.014 % $\text{Cr}_2(\text{SO}_4)_3$; < 0.2 % $\text{Al}_2(\text{SO}_4)_3$; < 0.03 % Na_2SO_4 and < 0.07 % CaSO_4 .

The waste waters are transported by special tankers to the dumping area, and there introduced into the tanker's screw-water at a travelling speed of 10 to 15 km/h. In this manner, the waste waters are quickly diluted with seawater. Six minutes after the dumping, the dilution was circa 1 : 1000; 65 minutes after dumping circa 1 : 10000; 650 minutes after dumping circa 1 : 100000 (Weichart, 1977). Through the addition of the sulphuric acid contained in the waste waters, the H^+ ion activity of the seawater is heavily increased and, thereby, the pH-Value is forced down. The FeSO_4 works in the same direction, because the Fe precipitates as Fe hydroxide. As the result of the pH change, other chemical changes in the seawater occur; for example, in the CO_2 system. Biologically it is likely that the intensive increase of the CO_2 partial pressure is particularly important, because the expiration of the CO_2 formed in the body will be rendered very difficult for animal organisms.

Waste waters from TiO_2 production are dumped at several positions in the North Sea (see Weichart, 1973 (a) and (b)) and also in other sea areas. Particularly careful investigations were made in the New York Bight: where, since April, 1948, large quantities of titanium waste waters have been dumped (see,

above all, Ketchum and Ford, 1948; as well as Redfield and Walford, 1951).

Investigations and Results

The most important physical processes and chemical changes in the dumping area and its vicinity were investigated with the SRV "Gauß" during the years 1969 to 1975. Moreover, the chemical state before the dumping was established during 1967. The largest part of the results have already been published (Weichart, 1972 (a) and (b), as well as 1975 (a) and (b)). The results of the pH measurements are described in this paper.

During our investigations, the horizontal as well as the vertical distribution of pH-value in the German Bight were determined. The measurement of the horizontal distribution was carried out at 5 m depth, because the strongest pH changes occur in the near-surface water layer, that is, not only because of the wastes but also as a result of photosynthesis and respiration.

The pH-values in the German Bight were really different at various seasons of the year. In autumn (including late summer) and early spring relatively low pH-values were found, because at these times of the year the organic compounds which had been built up by primary production (= photosynthesis) during the spring and summer are decomposed again, setting free CO₂. The lowest pH-values, apart from the titanium dumping area, were found in the vicinity of the Schleswig-Holstein coast; because it is there that the organic matter is decomposed

which reaches the German Bight via the Rivers Elbe and Weser. The vertical pH differences were low.

In spring and summer higher pH-values occurred within the euphotic layer (down to about 15 m depth) than in autumn, because owing to the strong primary production of the phytoplankton much CO_2 is taken up from the seawater and converted into organic compounds. The highest pH-values were found in May, June, and August. They were about 8.50. Such high pH-values can only appear in areas with a plentiful supply of nutrients (phosphate, nitrate, etc.) after a period of relatively quiet sunny weather conditions. The patchiness of phytoplankton distribution produces a corresponding micro structure of the pH distribution in the euphotic layer. Below the euphotic layer, the pH-value compared with the cold time of the year was only slightly raised.

The fresh screw-water of the wastes tanker showed, in comparison to the surrounding waters, a noticeably lower pH-value. One minute after dumping, the pH in the centre of the screw-water (5 to 10 m depth) was about 4.0. Ten minutes after dumping, the pH-value was about 6.1; and 100 minutes after dumping, about 7.5. The pH-value of the surrounding seawater lay between 8.15 and 8.30. With lower turbulence, i.e. calm sea, the dilution may take place more slowly; with strong turbulence, more quickly.

In the titanium dumping area, as well as within its near vicinity, flecks with clearly diminished pH-values were found

on several occasions. Probably, these originate from the acid titanium wastes. However, the pH-values observed in the "acid flecks", apart from the fresh (visible) titanium tanker screw-water, correspond to those which "naturally" occur in the South East German Bight. In certain cases, the pH differences which occurred naturally were so large that the influence of the acid wastes was not to be detected.

A steady increase in the acid concentration (reduction of pH-value) during the course of the years 1969 to 1975 could not be observed. Evidently, the acids are transported out of the German Bight into the open North Sea by residual currents. Moreover, the acid wastes dumped are neutralised by the CO₂ system of the seawater, which releases CO₂ into the atmosphere.

Illustrations

Owing to the high cost of printing, the partly coloured illustrations are attached to a limited number of copies only.

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