### C – CHEMICAL OCEANOLOGY

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### Analytical methods - CA

#### CA.01.

# INVESTIGATION OF THE SEWAGE POLLUTION ZONE IN THE MARINE COASTAL WATERS BY CHEMICAL AND BACTERIOLO-GICAL INDICES

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Oceanologia 1979, no. 11, pp. 113-128.

#### Abstract

The current situation regarding water pollution off the Polish central coast near sources of terestrial run-off is described, and the pollution load entering the sea via underwater sewage outfalls and river estuaries is defined. The results of studies on the range of terrestrial pollutant dispersal is compared with the directions and strength of the prevailing winds in this region. The long-term wind roses are of assistance in predicting how often similar conditions for the spread of pollution in coastal waters will exist at different times of the year.

Three sets of data concerning pollutant dispersal are presented: a) industrial pollutants, discharged into the sea by means of long, undersea outfalls (up to 800 m from the shore), b) municipal sewage, discharged into the sea from short outfall pipes (80 m offshore), and c) pollutants entering the sea with the waters of the river Parseta.

The test for the presence of excrement-type coli bacteria was found to be the most accurate of the currently available tests for detecting water pollution due to excreta. The name coli can be applied as an index of pollution not only to inland waters, but also to estuaries and offshore waters, provided the scale of the numerical comparisons used is always identical.

#### CA.02.

## THE APPLICATION OF WASTE SYNTHETIC FIBRES TO REMOVE OIL SPILLS FROM WATER SURFACES

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Oceanologia 1979, no. 11, pp. 139–153.

#### Abstract

The usefulness of waste synthetic fibres for removing oil spills from seawater surfaces is assessed. The capacity to absorb oil was referred to the surface properties of the fibres and their spatial arrangement in clumps of this waste. The papers of other authors discussing the application of fibrous sorbent materials for the removal of oil spills are quoted. A number of experiments were performed in which a sorbent obtained from the warp of spent automobile tyres as well as viscose and polyamide fibres was used to absorb crude oil and 'Lux 10' motor oil. The relationship between the experimental results and theoretical calculations was considered. The method of preparing the sorbent and its basic physico-chemical properties were given in an earlier paper [3].

Conclusions:

- 1. The results indicate that the surface properties of the fibres exert a considerable influence on their absorbent capacity when seawater and oil penetrate the fibre clumps together. When, however, all the fibres are in contact with the oil, the absorbent capacity depends on the sorbent structure alone, and the effect due to the fibre's surface properties can then be neglected. The quantity of oil absorbed rises with increasing fibre packing density, reaching a maximum within the range 0.15-0.30 g cm<sup>-3</sup> depending on the type of sorbent. This is lower than the theoretical value.
- 2. The most appropriate fibre packing density in sorbent barrages, mats or strips depends on the mechanical properties of the fibres and the required sorbent-oil binding strength. It is difficult to assess the sorbent packing density in the case of comminuted fibres; if this should be too low, considerable release of oil when gathering sorbent oil mixtures from the water surface is to be expected.
- 3. A lower fibre packing density enables water to penetrate the clump more rapidly, thereby impairing the oil absorbent capacity.
- 4. The best absorbence is achieved with a comminuted sorbent and a fairly viscous oil.
- 5. The sorbent capacity of commercial substances is usually given for the comminuted form. This will be very much lower when these substances are used in the form of sorbent barrages, mats, pads or strips. This fact should be taken into consideration when performing calculations concerning the removal of oil spills.

6. The sorbent obtained from the warp of spent automobile tyres is competitive even with such cheap sorbents as straw or sawdust, among other things because of its excellent absorbent properties and the fact that it can be recycled. Moreover, it is a far superior absorbent of oil products than either polyamide or viscose fibres.

#### CA.03.

THE ATMOSPHERE AS A SOURCE OF TRACE METAL INPUT TO THE GDAŃSK BASIN

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Oceanologia 1980, no. 12, pp. 43–58.

#### Abstract

The paper presents the results of analyses of cadmium, copper, mercury, lead and zinc in aerosols, rain water and dry fallout. Samples were taken at the weather stations at Hel and Gdynia, and in the Gdańsk Basin during research cruises in 1975–1976. The sampling procedures were worked out in accordance with WMO guidelines and their application to trace metal determinations.

Total mercury and its inorganic forms were analysed using the cold vapour technique. The organomercury content was obtained by subtracting the above amounts, and made up on average 67% of the total mercury flux in the dry fallout and precipitation.

The other metals were determined by AAS with electrothermal atomisation. All measurements were performed on a Beckman 1272 atomic absorption spectrophotometer.

The trace metal concentrations in ground-level aerosols (0.075  $\mu$ g Cd m<sup>-3</sup>, 0.12  $\mu$ g Cu m<sup>-3</sup>, 0.034  $\mu$ g Hg m<sup>-3</sup>, 1.2  $\mu$ g Pb m<sup>-3</sup> and 0.024  $\mu$ g Zn m<sup>-3</sup>) were approximately the same as those recorded over other water areas and lightly industrialised land areas.

In urban agglomerations the mean fluxes of metals carried by rain water were: Cd - 0.3, Cu - 2.34, Hg - 0.39, Pb - 4.61, Zn - 1.48  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>; at sea the corresponding values were: Cd - 0.07, Cu - 0.38, Hg - 0.36, Pb - 1.76, Zn - 0.59  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>.

The mean metal fluxes in the dry fallout at Hel and Gdynia were Cd – 0.65, Cu – 1.19, Hg – 1.9, Pb – 2.74, Zn – 0.64  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>, and in the Gdańsk Basin Cd – 0.09, Cu – 0.22, Hg – 0.07, Pb – 0.63, Zn – 0.38  $\mu$ g m<sup>-2</sup> h<sup>-1</sup>.

During the measurement period, the weather at Hel and Gdynia was very similar to that over the Gdańsk Basin, so that the data from both stations could be used to calculate the potential discharge of these metals into the sea in the shore zone. The average annual inflows of metals into the Gdańsk Basin were thus calculated at 38 tonnes Cd, 142.5 tonnes Cu, 60 tonnes Hg, 455 tonnes Pb and 171 tonnes Zn.

The air over the Gulf of Gdańsk was found to be a greater source of cadmium (1.8 times), mercury (1.6 times) and lead (3.8 times) than the river Vistula (Wisła). River discharge, however, 'supplies' far more copper and zinc to the Gdańsk Basin than does the air.

#### CA.04.

SPECTRAL METHODS IN WATER ANALYSIS

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Oceanologia 1981, no. 13, pp. 21–34.

#### Abstract

The world literature from 1975–1977 has been analysed with respect to the frequency with which various analytical techniques are used to detect trace metals in water. The merits, defects and limits of the following methods to detect the organic and inorganic forms of occurrence of trace metals are discussed: atomic absorption and fluorescence spectrometry, atomic emission spectrometry, X-ray fluorescence spectrometry, and a range of new techniques, *e.g.* PIXE (Proton Induced X-ray Excitation). In the 200–300 papers published each year on the identification of elements in water, more than half of the analytical techniques are based on atomic spectrometry or X-ray fluorescence spectrometry.

#### CA.05.

### THE DETERMINATION OF MERCURY IN SEA WATER AND BALTIC SEDIMENTS BY COLD VAPOUR AAS

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Oceanologia 1981, no. 13, pp. 77–92.

Abstract

The paper presents the results of mercury determinations in samples of Baltic water and sediments. Special attention was paid to the various chemical and physico-chemical forms of occurrence of this element. Both labile and stable forms were determined. Methodological examinations demonstrated the considerable influence of pH on the changes of the forms during the storage of the samples. In the Baltic an organically-bound stable form of mercury, linked quantitatively with the concentration of dissolved organic carbon, appears to be dominant.

The anthropogenic fraction and the annual discharge into the Baltic were estimated from the amounts of mercury in the sediment cores, as were the balance and the residence time in the Baltic. The calculated correlation coefficient was indicative of a precise relationship between the amount of mercury in the sediment samples and the quantities of other components (e.g. carbon, nickel).

The analytical methods used are described in detail.

#### CA.06.

### THE DETERMINATION OF MERCURY AT ULTRAMICROTRACE LEVELS IN WATER USING THE LOW-PRESSURE RING DISCHARGE

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Oceanologia 1981, no. 13, pp. 93–104.

#### Abstract

The ability of mercury to bind with protein favours its accumulation in living organisms and its bioconcentration in food chains, this latter process proceeding particularly well in aquatic food chains. In fish tissues mercury can reach concentrations 3–5 orders of magnitude greater than that of the surrounding water; hence the need to determine even very low amounts of mercury in water.

The paper describes the use of low-pressure ring discharge emission spectrometry for determining ultramicrotrace amounts of mercury in water. The detection limit achieved  $-0.1 \text{ mg dm}^{-3} \text{ Hg/H}_2\text{O}$  for distilled water - makes this a suitable method for examining the fine processes of mercury exchange a solution and its surroundings, *e.g.* between a solution and the walls of the vessels used in analytical techniques, or for studying

the exchange of mercury between the air and a water surface. At the ultramicrotrace level, these effects are the principal sources of errors when determining mercury in aqueous solutions.

Investigations carried out in Baltic seawater showed that the mercury content in the sea areas in question ranged from 30 to 60 mg dm<sup>-3</sup>. Sometimes, values as low as 10 or as high as 100 ng dm<sup>-3</sup> were recorded; in extreme cases, they were in excess of 350 ng dm<sup>-3</sup>.

It was very important as regards the method's sensitivity that the analytical line of the element to be analysed should be matched to the maximum sensitivity range of the spectral photomultiplier used for detecting the radiation, and that an appropriate buffer gas was used to fill the spectral lamp. Using helium as buffer rendered the technique more sensitive towards mercury.

#### CA.07.

#### DETERMINATION OF TRACE AMOUNTS OF MERCURY IN WATER BY GRAPHITE-SPARK SPECTROSCOPY

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Oceanologia 1981, no. 13, pp. 105–112.

#### Abstract

Preliminary results of research into the possibility of determining trace amounts of mercury using atomic emission spectroscopy with a graphite spark, and the initial, electrolytic release of mercury from the solution at the electrode. The experiments were performed on distilled water and substitute seawater contaminated with mercury. The detection limit of mercury in these types of water proves the practicability of this method for determining microtrace quantities of mercury in water. In comparison with electrogravimetry, the detection limit of mercury in water was improved by ca 4 orders of magnitude; compared to classic emission analysis (using thermal excitation sources) an improvement of one order of magnitude was achieved.

The method is not very time consuming, the analytical equipment is simple and the analyses can be performed by laboratory technicians – these are further advantages of this method.

#### CA.08.

EXCHANGE OF MERCURY BETWEEN WATER AND THE WALL OF A VESSEL AND ITS EFFECT ON THE RESULTS OF DETERMINATIONS

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Oceanologia 1981, no. 13, pp. 113–121.

#### Abstract

Determinations of ultramicrotraces of mercury in water are seriously affected by physical sorption and desorption of this metal at the walls of a container. This effect was investigated in glass, polyethylene and quartz vessels with different surface densities of mercury solutions in distilled water. Following long-term storage of an aqueous solution of mercury in containers of these materials, considerable changes in the mercury concentration in the solution were found to have occurred, due to both sorption and desorption of mercury at the walls of the container. These studies indicate that in the ultramicrotrace range, and especially in the submicrotrace range of mercury concentrations, substantial errors in determinations can occur due to the migration of mercury between the solution and the wall of the container used for collecting and storing the sample. These errors were found to be greatest when polyethlyene vessels were used. In containers made from this material, under favourable conditions the diurnal variations in mercury content in the ultramicrotrace range can be in excess of 50% of the original level.

The kinetics of mercury exchange between a solution and the walls of the vessel it is contained in are closely dependent on the surface density of the solution, the temperature of the material the vessel was made from, *etc.* 

Of the containers tested, those made of quartz glass are the most suitable for storing aqueous solutions containing mercury. The use of polyethylene vessels for this purpose considerably increases the risk of accidental errors caused by loss of mercury due to its migration from the solution to the wall of the container, or to the revsere process, in which mercury is desorbed from the walls of the vessel into the solution, thereby increasing its concentration.

#### CA.09.

### ASSAYING THE MERCURY LEVEL IN WATER BY THE LUMINES-CENCE METHOD

MARIAN STOŃ, HENRYK SZMACIŃSKI, JAN TROJANOWSKI Pedagogical University, Słupsk Oceanologia 1981, no. 13, pp. 123–129.

#### Abstract

The application of luminescence to determine the content of mercury in water is described. The qualitative analysis is founded upon the formation of rhodamine-mercury (RB–Hg) complexes in aqueous solutions which fluoresce over a range of visible light wavelengths. The absorption and fluorescence spectra of these complexes were measured, as was their stability in an extractant mixture (2:1 v/v benzene:diethyl ether).

The fluorescent intensity of these complexes was found to be linear in the range  $10^{-8}$  M $-5 \times 10^{-4}$  M mercury in water.

The measurements were carried out on substitute Baltic water and type B seawater. It was demonstrated that the detection limit could be lowered by concentrating the content of fluorescing complexes in the luminescing sample.

#### CA.10.

A STUDY OF THE COMPLEXATION REACTION OF MERCURY (II) WITH RHODAMINE B FROM THE POINT OF VIEW OF ITS UTILISATION IN ASSAYING MERCURY BY THE LUMINESCENCE METHOD

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Oceanologia 1981, no. 13, pp. 131–140.

#### Abstract

The conditions under which the complexation reaction between rhodamine B and Hg (II) is analysed with regard to its possible utilisation in the determination of small quantities of mercury in seawater by means of luminescence. 2:1 benzene:diethyl ether served as the extraction mixture. Absorption was measured with a Specord UV VIS spectrometer, luminescence with a specially assembled piece of apparatus, and pH with an LBS-66 pH-meter.

 $R_B$ -Hg (II) complexes were best extracted from the aqueous phase at pH 1–2. Extraction into the organic phase is also dependent on the concentration of chloride ions, which probably act as a supplementary ion. The best effects were achieved with 0.1–0.2 M aqueous solutions of NaCl.

The extraction mixture was saturated by the complex using a constant concentration of HgCl<sub>2</sub> ( $C_{Hg} = 2 \times 10^{-5}$  M), while optimum conditions

(pH = 1.5;  $C_{NaCl} = 0.15$  M) were achieved with a concentration of  $R_B$ –Hg (II)  $\approx 2 \times 10^{-4}$  M. Maximum extraction was *ca* 90%. Using a series of isomolar solutions and the equilibrium shift method, it was found that the reaction between RB and Hg (II) yielded a complex compound with the empirical formula  $[(HgCl_3)^- \times R_B^{\pm}]$ .

The results show that this reaction can be utilised in the quantitative determination of mercury in seawater using the luminescence technique.

#### CA.11.

#### EVALUATION OF SELECTED POLAROGRAPHIC TECHNIQUES FOR THE DETERMINATION OF URANIUM IN SEA AND INLAND WATERS

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Oceanologia 1981, no. 13, pp. 141-158.

Abstract

A review of the literature is presented on the determination of trace quantities of uranium by means of classical, rectangular and impulse polarography, differential impulse polarography and oscillopolarography. The possibility of adapting these techniques to detect micro- and nanogram quantities of uranium in various types of natural waters is indicated. The detectability, selectivity and accuracy of these methods are characterised, as are the techniques for uranium concentration and separation. In the description of classical (d.c.) polarography, attention is drawn to the possible use of a 0.01 M HNO<sub>3</sub> solution as principal electrolyte for assaying nanogram quantities of uranium in such waters. Impulse polarography with a principal electrolyte consisting of 2 M  $HClO_4$  and 0.06 M sodium tartrate appears to be the best of the a.c. techniques. The oscillopolarographic technique of determining uranium in inland waters deserves special attention, as it is extremely sensitive and quick. Having used it to detect uranium in 30 thousand samples of inland water, its author considers it to be superior to fluorimetry and colourimetry.

On the basis of this general assessment of polarographic methods, it is suggested that oscillopolarography and impulse polarography be implemented in serial analyses of uranium in natural waters.

#### CA.12.

#### GAS CHROMATOGRAPHIC DETERMINATION OF Zn, Cu AND Ni IN BOTTOM SEDIMENTS IN THE FORM OF DIETHYLDITHIOCARBA-MATE COMPLEXES

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Oceanologia 1981, no. 13, pp. 159–174.

#### Abstract

The conditions are described under which diethyldithiocarbamate (DEDTC) complexes of Zn, Cu and Ni can be analysed chromatographically in standard mixtures and samples of bottom sediments.

A Pye Unicam Model 104 gas chromatograph equipped with a flame ionisation detector (FID) was used in the experiments. Glass columns with internal diameters of 2 and 4 mm, 1.5, 1.8 and 3.0 metres in length were used. The carriers were Chromosorb W-HP and Gas-Chrom Q, covered to varying degrees with the stationary phases SF-30, OV-7, OV-101, QF-1, BBBT and Tenex.

The standard mixture containing DEDTC complexes of Zn, Cu and Ni was separated on 5% OV-101 with a mixed column packing containing 1:1 w/w 5% OV-101 + 5% QF-1. This mixed packing was also used in the quantitative analysis of the complexes. The linearity range for the relationship between peak area and mass of complex converted to metal was 10-200 ng for Cu and Ni, and 30-160 ng for Zn.

The analysis of sediment samples commenced with a 0.5 g portion of sediment being dried and then roasted at 500°C. The comminuted material was then digested in a Perkin Elmer pressure autoclave at 150°C for 40 minutes in a mixture, the content of which was given in the firm's instructions. Following digestion and expulsion of silicon in the form of  $SiF_4$ , the dry residue was dissolved in 10% HCl. After the addition of an aliquot of 30% H<sub>2</sub>O<sub>2</sub> and  $5000 \mu g$  La (III), Fe and Mn, which interfere in the chromatographic analysis, were co-precipitated by the addition of 25% $NH_3 \times H_2O$ . After being filtered off on a membrane filter, the precipitate was rinsed with  $NH_3 \times H_2O$  solution and deionised water. 3% NaDEDTC was added to the filtrate, previously purified of organic contaminants by extraction with 5:2 v/v CHCl<sub>3</sub>:(CH<sub>3</sub>)<sub>2</sub>CO. The complexes thereby formed were extracted with the same mixture as the pure reagent. On evaporating the solution to dryness on a water bath at  $80^{\circ}$ C, CHCl<sub>3</sub> and the internal standard solution n-dotriacontane were added to the residue, and the resulting solution analysed in the gas chromatograph: 0.5–1.0  $\mu$ l portions

were injected into the column packed with Cas Chrom Q with a mixed QF–1 + OV–101 stationary phase.

#### CA.13.

# ON THE DETERMINATION OF CADMIUM, COPPER, LEAD AND ZINC IN MARINE PARTICULATE MATTER BY ELECTROTHERMAL ATOMISATION

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Oceanologia 1984, no. 18, pp. 95–107.

Abstract

The effects of mineral and biological components of particulate matter and of the inorganic acids used to digest the particulate matter on ashing and atomisation in a graphite furnace have been studied. Interference from biological material, inorganic acids and membrane filter material during the determination of trace metals by flameless AAS are discussed.

#### CA.14.

INVESTIGATIONS INTO THE APPLICATION OF AN IMPREGNATED GRAPHITE ELECTRODE FOR THE ANALYSIS OF TRACE METALS IN SEA WATER BY ANODIC STRIPPING VOLTAMMETRY (ASV) (Communications)

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Oceanologia 1990, no. 28, pp. 129–137, (no abstract).

#### CA.15.

APPLICATION OF AMBERLITE XAD RESINS TO THE ISOLATION OF HUMIC SUBSTANCES FROM SEAWATER

WALDEMAR GRZYBOWSKI Institute of Oceanography, Gdańsk University, Gdynia JANUSZ PEMPKOWIAK Institute of Oceanology, Polish Academy of Sciences, Sopot Oceanologia 1992, no. 33, pp. 105–109.

Keywords: Humic substances, Seawater, Isolation method

#### Abstract

XAD-2 and XAD-8 resins were found to be equally efficient as sorbents of dissolved humic substances from seawater but the substances sorbed on the former were found more difficult to elute. UV–VIS and IR spectra of the isolated humic substances did not differ significantly, indicating the affinity of both resins to the same range of substances.

The influence of desorbents (solutions of  $NH_4OH$  and NaOH) on the quality of the substances was tested. After removal of excess base by vacuum evaporation ( $NH_4OH$ ) and ion exchange (NaOH), a higher level of nitrogen was found in the humic acids eluted with ammonium hydroxide, a fact attributable to the formation of ammonium salts of the humic substances. Irreversible sorption on the ion exchanger was the reason for the smaller proportion of the high molecular weight fraction in the substances eluted with sodium hydroxide.

#### CA.16.

A METHOD FOR DETERMINING FREE FATTY ACIDS (FTA) IN MARINE PLANKTON AND SEDIMENTS BY MEANS OF HIGH PER-FORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF THEIR P-NITROBENZYL ESTERS

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Oceanologia 1993, no. 34, pp. 57-68.

Keywords: Free fatty acids (FFA), p-nitrobenzyl esters, High performance liquid chromatography (HPLC), Marine plankton, Sediments

#### Abstract

A method for determining free fatty acid content in marine plankton and sediments by HPCL analysis of their p-nitrobenzyl esters has been developed. The acids were extracted from lyophilised samples of plankton or sediment with a 2:1 chloroform-methanol mixture. They were isolated from the remaining lipids by extraction with alkaline water

and reextraction, after acidification, with chloroform. The solvent was evaporated, the remaining substances dissolved in dichloromethane (DCM) and esterified with N,N'-dicyclohexyl-O-p-nitrobenzyl isourea (DcH-pNB-iU). The reaction mixture was separated on a silicagel pad using a cyclohexane-ethyl acetate mixture, the fractions containing the esters were evaporated, dissolved in an appropriate solvent and analysed by means of HPLC.

#### Chemical monitoring – CM

#### CM.01.

#### HUMIC SUBSTANCES IN THE BALTIC SEDIMENTS

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Oceanologia 1977, no. 7, pp. 105-120.

#### Abstract

The paper describes a method of rapidly separating humic substances from sediments and decontaminating them under conservative conditions. The sediment is first treated with 0.1 M Na<sub>2</sub>EDTA solution, then extracted with 0.2 M KOH.

If only alkaline extraction is used, a tenfold extraction with 0.5 M KOH is necessary – this was verified by determining the organic carbon content ( $C_{org}$ ) in the sediment after each extraction. The humic substances thereby obtained are separated into humic acids and fulvic acids in that their different solubilities in an acidic environment (pH 2) is made use of. The humic acids were purified by centrifugation, the fulvic acids on a column packed with Sephadex G-10.

The visible light spectrum of the humic acid solutions displays two points of inflexion – at 405 and 665 nm, whereas the fulvic acid spectrum is monotonic in this range. The UV spectrum for both humic and fulvic acids has an inflexion point at ca 280 nm.

In all the fractions analysed there are absorption bands due to the presence of hydroxyl, carbonyl, carboxyl and amino groups, and also to the peptide bonds in aromatic groups and polysaccharides.

Elemental analysis showed that the humic acids contained 53.94–56.61% carbon, 6.14–6.75% hydrogen and 5.74–6.44% nitrogen. The elemental composition of the fulvic acids was somewhat different: 46.68–47.32% carbon, 5.61–6.13% nitrogen and 7.35–7.77% hydrogen. No relationship between the shape of the IR spectra and the elemental composition of these compounds was found.

The increased extraction yield following the preliminary use of  $Na_2EDTA$  can be explained by the complexation of metallic ions by this strong ligand. The influence of EDTA on the structure of the silty minerals, principally

responsible for adsorbing humic substances in seawater, could also be of importance.

#### CM.02.

### CONTENTS OF OXYGEN AND NUTRIENTS IN THE FRONTAL ZONE OF THE BRAZIL AND FALKLAND CURRENTS

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Department of Oceanography, Sea Fisheries Institute, Gdynia

Oceanologia 1983, no. 14, pp. 167–186.

#### Abstract

The distribution of nutrients in the western Argentine Basin down to a depth of 2000 m is described; the area where the waters of the Brazil and Falkland Currents meet is subjected to particular scrutiny.

The steep pycnocline in this area hinders vertical mixing of waters, thus the surface layer is distinctly poor in nutrients. Wherever the pycnocline was steep, distinct concentration gradients were measured, whereas in places where the pycnocline was blurred, nutrient concentrations increased systematically to the detection limit, except in the case of nitrites, which were only occasionally found to occur below the pycnocline. The areas of highest phosphate and nitrate concentrations coincide with those where cyclonic vortices raise fertile abyssal waters in the frontal zone of these currents.

#### CM.03.

### HYDROCHEMICAL OBSERVATIONS AT AN ANCHORED STATION IN EZCURRA INLET

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Oceanologia 1984, no. 15, pp. 21-64.

#### Abstract

The measurements of dissolved oxygen, phosphates, silicates, nitrites and nitrates in the waters of Ezcurra Inlet are presented. They were made between 19 December 1977 and 10 March 1978 as part of the 2nd Antarctic Expedition of the Polish Academy of Sciences. The mean values during the observation period were (in  $\mu$ mol dm<sup>-3</sup>±1<sub> $\sigma$ </sub>): Si 82.2±1.8, P 1.96±0.12, NO<sub>2</sub><sup>-</sup>-N 0.17±0.02 and NO<sub>3</sub><sup>-</sup>-N 25.4±1.0, and the mean salinity at this time was 33.913 PSU. The proportion of soluble organic forms of phosphorus and nitrogen is no greater than 10% of their totals. Variations in concentrations of soluble nutrients and of oxygen depend on physical factors, principally winds and tides. Biological rhythms do not noticeably affect the changes in the oxygen or soluble nutrient contents, although they do become apparent in the seasonal variability of suspended phosphorus. The waters of Ezcurra Inlet do not form a stable gravitational structure, a situation favouring the equalisation of concentrations throughout the water column by the mixing factors. As these waters are permanently deficient in oxygen, they absorb it from the atmosphere.

#### CM.04.

## OCCURRENCE OF ORGANOMETAL COMPLEXES IN WATER OF THE BALTIC SEA

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Oceanologia 1983, no. 16, pp. 167-177.

#### Abstract

Samples of seawater and Vistula river water, taken at the stations shown in Fig. 2, were filtered through a Whatman GF/F glass filter. The concentrations of humic substances (DHS) and trace metals (Cu, Zn, Fe, Pb, Ni) were then determined in the water before and after passing it through a column packed with Amberlite XAD-2 (Serva) (Fig. 1). The DHS concentration in the seawater samples was found to vary between 1.21 and  $2.45 \text{ mg dm}^{-3}$ . The respective concentrations of Fe, Zn, Ni, Pb and Cu were: 1.6–3.6  $\mu g dm^{-3}$ ; 5.1–73.8  $\mu g dm^{-3}$ ; 1.9–11.7  $\mu g dm^{-3}$ ; 0.10–0.43  $\mu g dm^{-3}$  and 1.1–4.1  $\mu g dm^{-3}$  (Tab. 2). In the water samples passed through the Amberlite XAD-2 column, the concentrations of these trace metals were much lower, the respective mean reductions in Fe, Zn, Ni, Pb and Cu concentrations being 41, 38, 40, 34 and 28% in surface water and 47, 43, 34, 48 and 32% in near-bottom water (Tab. 3). This effect was attributed to the sorption of organometal complexes on Amberlite XAD-2. These values thus characterise the proportion of organometal complexes stable at pH 2.0 in the overall concentration of these metals in seawater. This interpretation is supported by the determinations of metal concentrations in water before and after passing through a column of Amberlite XAD-2 (Fig. 1). The elemental composition of DHS (Tab. 4) and their IR spectra (Fig. 3) indicate

the presence of functional groups capable of acting as donors in complexes with trace metals.

#### CM.05.

#### THE OCCURRENCE OF MERCURY IN THE SOUTHERN BALTIC SEA

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Institute of Meteorology and Water Management, Maritime Branch, Gdynia

Oceanologia 1984, no. 18, pp. 109–116.

#### Abstract

The results of systematic investigations on the occurrence of mercury in the southern Baltic, (Polish economic zone) are presented. Unfiltered seawater, sampled in 1978–1981 from 10 stations selected for international and national pollution monitoring in the Baltic, was analysed. Total mercury concentration was determined by flameless AAS, after mineralisation of organic mercury compounds.

#### CM.06.

THE INFLUENCE OF LAKE ŻARNOWIEC ON THE OUTFLOW OF IONS WITH THE PIAŚNICA RIVER WATERS

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Oceanologia 1985, no. 20, pp. 85–95.

Keywords: Outflow of ions, Lake Zarnowiec, Piaśnica River

#### Abstract

An attempt has been to estimate the influence of Lake Zarnowiec on the chemical composition of waters flowing with the Piaśnica River through the Lake to the Baltic Sea. To do this, a four-year period of measurements of feeding the Lake with chemical components and their outflow was utilised.

#### CM.07.

DISTRIBUTION OF SOME NUTRIENTS IN THE SOUTHERN BALTIC IN AUG/SEPT 1983 IN RELATION TO CONDITIONS IN THE TWO PREVIOUS YEARS

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Oceanologia 1985, no. 21, pp. 77–97.

Keywords: Nutrient distribution, Nitrates, Nitrites, Phosphates, Silicates, Southern Baltic, 1981–1983

#### Abstract

This paper presents the results of investigations carried out on board r/v 'Profesor Siedlecki' in August/September 1983 in relation to the hydrological conditions during this period. Changes in nutrient concentrations (phosphate, nitrate, nitrite, silicate) in 1981–1983, taking into account the effects of the inflow from the North Sea in October 1982, are discussed. The measurements were carried out in both the open sea and the coastal zone of the southern Baltic.

#### CM.08.

OXYGEN AND THERMOHALINE CONDITIONS IN THE POLISH FISHING ZONE IN 1979–1983

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Oceanologia 1990, no. 29, pp. 3–25.

Keywords: Baltic water temperature, Salinity, Water saturation with oxygen

#### Abstract

The article presents the thermohaline and oxygen conditions in the Polish fishing zone in the period 1979–1983. The discussion is based on the results of investigations carried out according to stage I of the Baltic Monitoring Programme within the framework of the Helsinki Convention. Long-term trends in fluctuations of water temperature, salinity and oxygen saturation induced by natural and anthropogenic factors are also presented.

#### CM.09.

SEASONAL FLUCTUATIONS AND LONG-TERM TRENDS OF NUTRI-ENT CONCENTRATIONS IN THE POLISH ZONE OF THE BALTIC SEA

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Oceanologia 1990, no. 29, pp. 27–50.

Keywords: Baltic Sea, Nutrients, Eutrophication

#### Abstract

The article presents the state of productivity of the Polish zone of the Baltic Sea assessed on the basis of 5-year (1979–1983) investigations carried out within the framework of the Helsinki Convention according to stage I of the Baltic Monitoring Programme. Seasonal fluctuations in phosphorus, nitrogen and silicon compound concentrations in the Polish zone of the Baltic Sea and long-term variations in phosphate and nitrate concentrations in the entire Baltic Sea indicated the progressive eutrophication of this basin. Eutrophication has also affected other chemical properties of the environment, such as oxygen conditions and water pH.

#### CM.10.

COPPER CHLORINS IN THE WATER AND SEDIMENTS OF THE BALTIC SEA

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Oceanologia 1992, no. 33, pp. 111-129.

Keywords: Copper, Copper chlorins, Copper complexes, Organic copper complexes, Marine environment, Baltic Sea

#### Abstract

Copper chlorins, complexes of copper with the most abundant derivatives of chlorophyll a in this environment, were investigated in the water and sediments of the Baltic Sea using HPLC and LC–MS. Extracts of the organic substance adsorbed from water on XAD–2 resin revealed the presence of allo-phaeophytins a, oxygenation products of Cu-phaeophytin a. The sediments contained small amounts of Cu-phaeophytin a and Cu-pyrophaeophytin a. The results indicate that in the investigated area copper is incorporated into the chlorin complexes of phytoplankton origin in the surface water and released from the complexes above the bottom or within the sediments.

#### CM.11.

THE COMPLEXING CAPACITIES OF HUMIC SUBSTANCES ISO-LATED FROM BALTIC SEDIMENTS AND THEIR MOLECULAR WEIGHT FRACTIONS TOWARDS COPPER(II) AND IRON(III)

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Oceanologia 1993, no. 34, pp. 39–47.

Keywords: Complexation, Copper(II), Iron(III), Humic substances

Abstract

Humic substances were isolated from sediments collected from the Gdańsk Deep, separated into humic acids and fulvic acids, and further separated into molecular weight fractions by ultrafiltration. The respective complexing capacities of the fractions towards copper(II) and iron(III) lie in the 0.067–0.240  $\mu g m g^{-1}$  and 0.094–0.240  $\mu g m g^{-1}$  ranges. The complexing capacity increased with decreasing molecular weight of the fractions. Examination of the IR spectra of humic substances and their precipitates obtained after addition of excess metals revealed that the absorption band at 1710 cm<sup>-1</sup> (carbonyl of carboxylic groups) had shifted to 1600 cm<sup>-1</sup> (carboxylate ions), indicating the participation of carboxyl groups in the bonding of metal ions. The decreasing intensity of the DTG peak at 365°C supported this conclusion.

#### CM.12.

THE HYDROCHEMICAL AND BIOLOGICAL IMPACT OF THE RIVER VISTULA ON THE PELAGIC SYSTEM OF THE GULF OF GDAŃSK IN 1994. PART 1. VARIABILITY IN NUTRIENT CONCENTRATIONS

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Oceanologia 1995, no. 37 (2), pp. 181–205.

Keywords: Baltic Sea, Nutrients, Vistula impact, Seasonal/spatial variability

#### Abstract

The paper discusses the physical and biological factors as well as the water/nutrient discharges by the river Vistula affecting nutrient distribution in the Gulf of Gdańsk in 1994. Seasonal and spatial variability in nutrient distribution is discussed with reference to the biological cycle in the coastal marine ecosystem and with respect to seasonal variability in water/nutrient discharges by the river. The greatest discharge of nutrients, with extremely high concentrations of nitrates, was recorded in April 1994. Powerful water dynamics, mainly wind-induced, are depicted as a factor responsible for the transport/transformation of riverine water. Separate mini-ecosystems, characterised by distinguishable chemical, physical and biological parameters, were found. High concentrations of ammonia in July may have been related to its regeneration by abundant zooplankton. Low silicate concentrations in November may have resulted from a diatom bloom.

#### CM.13.

SHORT-TERM VARIATIONS IN THE CONCENTRATIONS OF SUSPENDED PARTICLES, CHLOROPHYLL a AND NUTRIENTS IN THE SURFACE SEAWATER LAYERS OF THE GDAŃSK DEEP

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Oceanologia 1995, no. 37 (2), pp. 249–284.

Keywords: Particles, Chlorophyll a, Nutrients, Microlayer, Gdańsk Deep

#### Abstract

An important interface between the atmosphere and sea, the sea-surface microlayer is a collection phase for many natural and anthropogenic materials, serving both as a source and a recipient of materials from the atmosphere and the water column.

Samples of sea-surface microlayer and subsurface bulk water were collected at short time intervals (every 1 h and every 4 h) in two periods: 2–6.06.1992 and 30.04–4.05.1994 and analysed for particle concentration with a Multisizer II Coulter Counter.

The results present diurnal variations in particle numbers and their distribution functions. The data illustrate the effect of the chlorophyll a and nutrient contents on particle concentration.

Both particle concentration and chlorophyll a content underwent periodic fluctuations. Maximum values were recorded in the morning and afternoon hours.

#### CM.14.

#### SELECTED PROPERTIES OF DIFFERENT MOLECULAR SIZE FRAC-TIONS OF HUMIC SUBSTANCES ISOLATED FROM SURFACE BALTIC WATER IN THE GDAŃSK DEEP AREA

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Institute of Oceanography, Gdańsk University, Gdynia

Oceanologia 1996, no. 38 (1), pp. 33–47.

Keywords: Humic substances, Baltic water, Heavy metals, Complexation

#### Abstract

Humic substances were isolated from surface Baltic water in the Gdańsk Deep area and fractionated by ultrafiltration on membrane filters of pore sizes 1000, 5000 and 10 000 Daltons. 97% of the material obtained was smaller than 10 000 D. The fractions were characterised by UV-VIS and IR spectroscopy, and analysed for elemental composition and functional group concentration. The nitrogen and phenolic hydroxyl group concentrations confirmed the autochthonous origin of the fractions. The aromaticity of the molecules was found to increase with molecular size, and the greatest saturation of aromatic rings with carboxyl groups was found in the fraction smaller than 1000 D. Complexation capacity was not directly connected with molecular size. All the fractions possessed a larger capacity for lead than cadmium, the complexation of the latter being detected only in the < 1000 D fraction.

#### CM.15.

VARIABILITY IN NUTRIENT DISTRIBUTION IN THE POMERANIAN BAY IN SEPTEMBER 1993

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Oceanologia 1996, no. 38 (2), pp. 195–225.

Keywords: Baltic Sea, Nutrients, Odra impact, Spatial variability

Abstract

Physical and biological factors as well as water/nutrient discharges from the river Odra (via the Szczecin Lagoon and the rivers connecting the Lagoon with the Pomeranian Bay) were found to affect nutrient distribution in the Pomeranian Bay in September 1993. Other factors influencing this distribution included the eutrophic waters of the Greifswalder Bodden, and physical phenomena such as upwelling and the pulsating nature of the river Świna's outflow. The dynamics of the water are thought to be a significant factor in the transport/transformation of riverine water. A separate 'mini-ecosystem', characterised by distinct chemical, physical and biological parameters, was recorded.

#### CM.16.

PRELIMINARY RESULTS OF DISSOLVED ORGANIC CARBON CONCENTRATION MEASUREMENTS IN THE VISTULA RIVER MOUTH USING HIGH-TEMPERATURE CATALYTIC OXIDATION (Communications)

WALDEMAR GRZYBOWSKI

Institute of Oceanography, Gdańsk University, Gdynia

Oceanologia 1996, no. 38 (3), pp. 395–403.

Keywords: Salinity, Dissolved organic carbon, High-temperature catalytic oxidation, Gulf of Gdańsk

#### Abstract

Some 100 measurements of dissolved organic carbon (DOC) concentrations were made in the water in the Vistula river mouth area using high-temperature catalytic oxidation. The results ranged from 4.8 to 22.4 mg dm<sup>-3</sup>. No relationship was detected between DOC and salinity within the 0.9–7.6 PSU salinity range.

Environmental pollution studies - CP

#### CP.01.

### STUDIES OF THE DISCHARGE OF NUTRIENT SUBSTANCES INTO THE BALTIC BY THE RIVER VISTULA

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Oceanologia 1977, no. 7, pp. 121–147.

Abstract

This paper gives the results of two-year studies to determine the characteristics of the discharge of nitrogen and phosphorus compounds into the Baltic with the Vistula river waters. The investigations covered the period from 20th January 1972 to 28th March 1974. Samples of river water were collected twice a week at three stations in a cross section of the Vistula at Tczew, about 15 km from the river mouth. The following forms of bound nitrogen were measured in the samples: total nitrogen by the Kjeldahl method (N-total), total dissolved nitrogen (N-total diss.), ammonium nitrogen (N-NH<sub>4</sub>), nitrate nitrogen (N-NO<sub>3</sub>) and nitrite nitrogen  $(N-NO_2)$ . The following forms of nitrogen were obtained by calculation: suspended nitrogen (N-susp) – from the difference between N-total and N-total diss., organic nitrogen (N-org) – from the difference between N-total and N-NH<sub>4</sub>, dissolved organic nitrogen (N-org diss.) - from the difference between N-total diss. and N-NH<sub>4</sub>, inorganic nitrogen (N-inorg.) – by summing N-NH<sub>4</sub>, N-NO<sub>3</sub> and N-NO<sub>2</sub>, bound nitrogen - by summing N-total, N-NO<sub>3</sub> and N-NO<sub>2</sub>. The phosphorus compounds measured were total phosphorus (P-total), dissolved phosphorus (P-diss.) and phosphate phosphorus  $(P-PO_4)$ . The following forms were calculated: seston phosphorus (P-sest) – from the difference between P-total and P-diss., dissolved organic phosphorus - from the difference between P-diss. and  $P-PO_4$ .

#### CP.02.

THE INPUT OF MERCURY COMPOUNDS WITH THE WATERS OF THE RIVER VISTULA

ANNA BRZEZIŃSKA, TERESA BOGACKA, REGINA TAYLOR, ANNA TRZOSIŃSKA Institute of Meteorology and Water Management, Maritime Branch, Gdynia Oceanologia 1979, no. 11, pp. 85–97.

#### Abstract

The paper presents the results of a two-year investigation (1974–1976) into the content of mercury compounds in the Vistula at the 69th, 509th, 926th and 941st kilometres of the river's course. The determinations were done in two separate laboratories using cold-vapour atomic absorption spectrophotometry and unfiltered water samples. Fish caught in the lower Vistula were also taken into account in that an average sample of the entire body was analysed.

The average total mercury concentration in the water was 1.01  $\mu$ g dm<sup>-3</sup> at Kraków, 0.89  $\mu$ g dm<sup>-3</sup> at Warsaw, 0.83  $\mu$ g dm<sup>-3</sup> at Kiezmark and 0.85  $\mu$ g dm<sup>-3</sup> at Świbno. The mean content of organomercury compounds made up *ca* 70% of the total at all the river sections, except near its mouth, where this level fell to 55%. The level of mercury in the Vistula did not fluctuate regularly according to season or flow rate. On the basis of the measurements made at Kiezmark and Świbno, the total amount of mercury carried annually into the Gulf of Gdańsk is of the order of 30 tonnes.

The determination of total mercury in fish indicates that a relationship exists between the amount of accumulated metal and the species and age of individual fish. The largest quantities of mercury were found in vimba, which feed on benthic fauna. In other species (bream, roach, vendace, lamprey, eel and pike) the mercury content lay between 0.18 and 0.96 mg per kg.

The results of this study indicate that the mercury content in the Vistula should be monitored on a regular basis.

#### CP.03.

## TRANSPORT OF PESTICIDES TO THE SEA BY THE RIVER VISTULA

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Institute of Meteorology and Water Management, Maritime Branch, Gdynia

Oceanologia 1979, no. 11, pp. 129–138.

#### Abstract

In 1972–1974 the Institute of Meteorology and Water Management carried out a study of pesticides in the lower Vistula. These substances included polychlorine insecticides (the DDT complex, methoxychlor and lindane) and herbicides derived from chlorophenoxyacetic acids (2,4–D and MCPA).

The concentrations of insecticides in the water reached 2.5  $\mu$ g dm<sup>-3</sup>; on average they were of the order of a few to 11–20 ng per litre. The maximum

concentrations were recorded in summer, when these compounds were being used in agriculture. The mean annual concentrations were highest in the first study year, subsequently dropping by 30–80%, probably because of the restrictions imposed on the use of polychlorine insecticides in Poland. The mean annual loads carried by the Vistula thus fell in successive years of this study by 15–80%. The quantity of pesticides carried right down to the sea comprised only a small percentage of the annual consumption of these compounds in the Vistula catchment area. In 1972, this was 0.085–0.85%, depending on the compound.

The remnants of polychlorine insecticides in fish bodies varied from undetectable amounts to a few ppm, depending on the species and age of the fish. No relationship between the concentration of pesticides and season could be discerned.

Herbicides occasionally occurred in Vistula waters, the average concentration being  $ca 0.3 \ \mu \text{g dm}^{-3}$ .

Of all these pesticides examined, only DDT presented any danger to the Vistula's aquatic ecosystem. The load of this contaminant carried into the sea is subject to immense dilution and cannot present any immediate danger to marine organisms. The withdrawal of DDT from general use means that the level of DDT and its metabolites in surface waters will fall, as will their load entering the sea.

#### CP.04.

### THE INPUT OF ORGANIC MATTER TO THE BALTIC FROM THE RIVER VISTULA

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Oceanologia 1980, no. 12, pp. 79–98.

#### Absctract

The contents of the following substances were determined once a week throughout 1977: suspended matter (SM); organic carbon in suspended matter (POC); humic substances in suspended matter (PHS), including fulvic acids (PFA) and humic acids (PHA); dissolved organic carbon (DOC); dissolved humic substances (DHS), including fulvic acids (DFA) and humic acids (DHA). The mean weekly mass of organic carbon and humic substances entering the Baltic Sea with the waters of the river Vistula was calculated (Tab. 1) from the average weekly Vistula flow rates (Fig. 1). The concentrations of SM, POC and the percentages of POC in SM are shown in Fig. 2. Fig. 3 gives the concentrations of PHS and PFA and the percentage of PFA in PHS. The percentage of PHS in the suspended organic matter and of DHS in the dissolved organic matter are illustrated in Fig. 5. Fig. 4 gives the concentrations of DOC, DFA and DHA. The mean monthly and annual concentrations of organic carbon and humic substances are set out in Tab. 2. These data served to calculate aspects of the organic carbon and humic substance balance in the Baltic Sea (Tab. 3). The physicochemical properties of humic substances are characterised on the basis of their elemental composition (Tab. 4), IR spectra (Fig. 6), VIS spectra (Fig. 7) and UV spectra (Fig. 8).

#### CP.05.

THE THREAT TO THE MARINE ENVIRONMENT FROM HEAVY METALS

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Oceanologia 1981, no. 13, pp. 9–20.

Abstract

The paper describes the sources of heavy metals, their paths of penetration to the marine environment and their effect on this, on the living resources of the sea and on human health. The latest data on the penetration of mercury, lead, copper, zinc and cadmium into the air, surface waters and soils are compared with the national (Polish) and world production of these metals.

It is demonstrated that the long period of time elapsing from the entry of a metal to the environment to the response of the ecosystem to its presence makes it difficult to establish the exact cause-effect relationship and thus to afford the ecosystem adequate protection. Important chemical and biological transformations undergone by these metals are given, as are their organic and inorganic compounds at various trophic levels in the marine environment.

#### CP.06.

THE RUNOFF OF NITROGEN AND PHOSPHORUS COMPOUNDS FROM SELECTED AGRICULTURAL AREAS IN THE VISTULA AND ODER DRAINAGE BASINS

REGINA TAYLOR Institute of Meteorology and Water Management, Maritime Branch, Gdynia Oceanologia 1984, no. 18, pp. 135–148.

#### Abstract

Systematic studies on the dynamics and extent of runoff of phosphorus and nitrogen compounds from selected agricultural areas in the Vistula and Oder drainage basins not possessing point pollution sources have been carried out. The data obtained permitted determination of the critical conditions under which large loads of fertilisers are transported by river to the sea. The size of these loads in a given area depends on the humidity conditions there. The coefficients of unit runoff also depend on physiography and degree of agricultural utilisation of the area.

#### CP.07.

VARIATIONS IN THE CHEMICAL COMPOSITION OF SURFACE WATERS TRANSPORTED TO THE BALTIC SEA WITH THE RIVER REGA IN THE PERIOD 1964–1975

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Oceanologia 1985, no. 20, pp. 69–83.

Keywords: Surface waters, Chemical composition, Baltic Sea, Rega River

#### Abstract

An attempt has been made to estimate the increase in pollutant levels of surface waters and of losses of fertiliser components during two periods differing in the intensity of fertilisation. To do this, the results of hydrological-chemical investigations carried out in the River Rega catchment area from January 1964 to December 1968 (1st period) and from May 1973 to April 1975 (2nd period) were utilised.