MASTER

THE DISTRIBUTION OF SOME CHEMICAL ELEMENTS
BETWEEN DISSOLVED AND PARTICULATE PHASES IN THE OCEAN

Report to the Atomic Energy Commission on Contract AT(II-I)3566

AEC Report No. C00-3566-4

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Introduction

This report summarizes our work during the period August 1972 to April 1973.

We have continued our investigations on the Cariaco Trench samples collected during cruise 60 of the R/V Atlantis II during August 1971, and we have established procedures for the determination of Pb^{210} in both the dissolved and particulate matter of the ocean. Additionally, we have continued investigations on the use of volatile-chelate-isotope-dilution mass spectrometry for the determination of some more elements in sea water.

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SOME RECENT DATA FROM THE CARIACO TRENCH

In our progress report of last year, we presented some evidence to suggest that the temperature of the deep water in the Cariaco Trench is increasing with time.

During the last year, we have obtained additional hydrographic data from both K. Fanning (of Univ. of Rhode Island) and R. Presley (of Texas A&M University).

The U.R.I. data is complicated by the fact that in all of the deep casts the bottom bottle shows a temperature that is about 0.02° to 0.06° lower than the bottle above. Presumably this represents a consistently low reading from a single thermometer. If the results from the bottom bottle are ignored and the remaining potential temperatures in the bottom 200 meters of the water column are averaged, then the mean potential temperature recorded by the U.R.I. team from a 1968 cruise lies between that of Richards taken in 1965 and Brewer in 1971.

The mean potential temperatures in the bottom 200 meters from five separate cruises are shown in figure 1. It is clear that the deep water of the Cariaco Trench is warming with time, and the deep water cannot be considered to be in a steady state condition. If the increase in the deep water temperature is due entirely to geothermal heating, then the heat flux would have to be of the order of $8\mu \text{ cal cm}^{-2} \text{ sec}^{-1}$. No heat flow measurements have been reported for the Cariaco Trench, but

this value appears to be higher than might be expected, and some other source of heat, perhaps from downward heat flux from the surface or anaerobic oxidation processes may be involved.

Whatever the source of the heat, it is apparent that at some time in the past a source of colder fresher water was available to fill the deep parts of the basin. The most likely source of this water is in the Antarctic intermediate water which flows through the Caribbean.

Radiocarbon data obtained for us by Dr. G. Ostlund are shown in Table 1. The data are given as ΔC^{14} where

$$\Delta C^{14} = \delta C^{14} - [2\delta C^{13} + 50] \left[1 + \frac{\delta C^{14}}{1000} \right]$$

(δC^{14} is the part per mille deviation from the N.B.S. oxalic acid standard, and δC^{13} is the part per mille deviation from the Peedee Belemnite standard.)

Pre-nuclear, pre-industrial surface ocean water had a Δ value of about -50, and the mid water values between 700 and 1100 meters would suggest a closed-system age of less than 200 years. (A Δ value decrease of -20% would occur for about 160 years of radioactive decay). However, the near bottom values of about -40% suggest a recent influx of surface C^{14} . There is no data to suggest that this influx is associated with a renewal of the bottom water, and the bottom water C^{14} may be affected by the solution of carbonate tests of recent surface origin or the anaerobic oxidation of recent organic matter that has sunk quickly to the bottom.

The inflection in the ΔC^{14} data with depth that occurs at 300-400 meters corresponds to the oxygen zero boundary. From the reported errors, it is difficult to have confidence that the inflection is real, but it may indicate that a slightly increased flux of C^{14} (over that determined by vertical diffusion) is taking place at this boundary, associated with the flux of precipitated particulate iron and manganese.

We plan to continue our investigations of this trench during the coming year.

TABLE I
CARIACO TRENCH C-14 DATA

Depth (m)	ΔC^{14}
25	125 ± 10
100	80 ± 7
200	-5 ± 10
300	-59 ± 12
400	-44 ± 6
500	-58 ± 6
750	-71 ± 6
900	-70 ± 10
1100	-65 ± 10
1250	-43 ± 10
1350	-38 ± 10

Figure 1

AVERAGE POTENTIAL TEMPERATURE VERSUS TIME IN
BOTTOM 200 METERS OF CARIACO TRENCH

List of Publications and Reports

Supported by Contract AT(11-1)-3566
Formerly AT(30-1)-4150

NYO-4150-1   Sachs, P. L. and D. W. Spencer (1970)
In situ measurement of light scattered from a laser beam
compared to suspended particulate concentrations derived
from concurrently collected samples

W. H. O. I. Technical Report

NYO-4150-2   The distribution of some chemical elements between dissolved
and particulate phases in the ocean

Report to AEC on Contract
AT(30-1)-4150, 1969-70

NYO-4150-3   Turner, J. S., T. G. Shirtcliffe and P. G. Brewer (1970)
Variations of transport coefficients across density
interfaces in multiple diffusive systems

Nature, 228, 1083

NYO-4150-4   Spencer, D. W., D. E. Robertson, K. K. Turekian and
T. R. Folsom (1970)
Trace element intercalibrations and profiles at the
GEOSECS test station in the north east Pacific Ocean

J. Geophys. Res., 75, 7688

NYO-4150-5   Brewer, P. G. and D. W. Spencer (1970)
Trace element intercalibration study

W. H. O. I. Technical Report
No. 70-62

NYO-4150-6   Brewer, P. G. and D. W. Spencer (1971)
Colorimetric determination of manganese in anoxic waters

Limnol. & Ocean., 16, 107

List of Publications, cont.

- NYO-4150-7   Spencer, D. W. and P. G. Brewer (1971)
Vertical advection, diffusion and redox potentials as
controls on the distribution of Mn and other trace
metals dissolved in waters of the Black Sea

J. Geophys. Res., 76, 5877
- NYO-4150-8   Spencer, D. W., P. G. Brewer and P. L. Sachs (1971)
Aspects of the distribution and trace element composi-
tion of suspended matter in the Black Sea

Geochim. et Cosmochim. Acta,
36, 71
- NYO-4150-9   Distribution of some chemical elements between dissolved
and particulate phases in the ocean.

Report to AEC on Contract
AT(30-1)-4150, 1970-71
- C00-3566-1   Brewer, P. G. and D. W. Spencer (1972)
The distribution and flux of some trace elements between
dissolved and particulate phases in the Black Sea

AAPG Memoir, E. T. Degens
and D. A. Ross, eds. (in press)
- C00-3566-2   Brewer, P. G., D. W. Spencer and D. E. Robertson (1972)
Trace element profiles from the GEOSECS test station in
the Sargasso Sea

Earth & Planet. Sci. L.
(in press)
- C00-3566-3   Distribution of some chemical elements between dissolved
and particulate phases in the ocean.

Report to AEC on Contract
AT(II-I)-3566, 1971-72.
- C00-3566-4   Distribution of some chemical elements between dissolved
and particulate phases in the ocean

Report to AEC on Contract
AT(II-I)-3566, 1972-73.
- C00-3566-5   Brewer, P.G., and J. W. Murray (1973). Carbon, nitrogen
and phosphorus in the Black Sea.

Deep Sea Res. (in press)

PRELIMINARY REPORT ON THE TRACE METAL COMPOSITION
OF SUSPENDED MATTER IN THE CARIACO TRENCH

Introduction

Particulate matter samples were collected during cruise #60 of the R/V Atlantis II to the Cariaco Trench. Samples were collected in 30 l. P.V.C. Niskin bottles and filtered through 0.5 μ pore size pre-weighed nucleopore filters. In figure 1, the profile of dry weight of total suspended matter is shown. The data range from a high value of about 2.0 mg/kg at the surface to a minimum of 0.2 mg/kg between 400 - 1200 m. There appears to be a slight increase close to the bottom.

We have begun analysis of these samples using the neutron activation analysis procedure described in Spencer et al. (1972). In this report, we will present some of the preliminary results of these analyses.

Results

The particulate Mn data are shown in figure 2. There is some scatter in the surface water with a mean value of about 45 ng/kg. The concentration increases rapidly below 200 m and reaches a well defined maximum of 1300 ng/kg at 300 m. From 300 m to the bottom, the particulate Mn values are uniformly low, averaging about 4 to 5 ng/kg. The particulate La profile (figure 3) is very similar to the total particulate matter profile (figure 1), indicating that the same processes control the distribution of these two variables.

Discussion

In a few weeks, we will have additional data for Fe, Co, Hg, Sc, Zn, Sb and Cr. At that time, a thorough analysis of the data will be undertaken. However, two preliminary points can be made at this time.

1. In figure 2, the values for dissolved Mn (taken from Brewer, AEC Report for 1971) are plotted for comparison with the particulate Mn data. Both sets of data show similar features as the dissolved and particulate Mn profiles in the Black Sea (Spencer et al. 1972). In the Cariaco, as in the Black Sea, both profiles show a sharp break at 300 m where the transition from an oxidizing to a reducing environment takes place. It appears likely that similar processes are operating in both the Cariaco Trench and the Black Sea. That is the upward mixing of divalent Mn from the reducing to the oxidizing environment, the precipitation of MnO_2 at the interface, and the settling and dissolution of this precipitate. The abrupt change in redox potential is the chemical driving force, and advection and diffusion control the dynamics of the system.

These data will be more difficult to model than the Black Sea data because of the difficulty in estimating the vertical velocity in the Cariaco Trench.

2. Dr. Brian Price (University of Edinburgh) was a guest investigator on this cruise, and we provided him with laboratory equipment and samples in order to undertake an intercalibration of our data. Dr. Price analyzed his samples using a X-ray fluorescence technique, and his data

provide a valuable comparison for our neutron activation data. In Table 1, Prices' data (personal communication) are compared with our own. There is excellent agreement for values above 0.01 $\mu\text{g/kg}$ which is the limit of sensitivity of the X-ray fluorescence technique. The analyses in this comparison were done on separate samples.

TABLE 1

<u>Eastern Basin</u>			<u>Western Basin</u>		
<u>Depth (m)</u>	<u>Edinburgh</u>	<u>Woods Hole</u>	<u>Depth</u>	<u>Edinburgh</u>	<u>Woods Hole</u>
5	0.02 $\mu\text{g/kg}$	0.0082 $\mu\text{g/kg}$	5	0.07	0.0703
50	0.04	0.0439	25	0.02	
100	0.02	0.0312	100	0.05	0.0645
200	0.24	0.3567	150	0.03	
320	0.01	0.0078	250	0.11	0.188
330	nd	0.0094	280	0.13	0.137
340	nd	0.0050	300	0.71	0.948
600	0.01	0.0048	310	0.54	0.659
1300	0.01	0.0079	350	0.49	0.772
1350	0.01	0.0211	400	0.02	0.0059

Fig. 1

Figure 2

Figure 3

DETERMINATION OF LEAD-210 IN SEA WATER

During the last year, we have bought and installed two silicon surface-barrier detectors which are currently attached to a 1024 channel pulse height analyzer. We have been working to establish methods for the determination of Pb^{210} in both the dissolved and particulate states in sea water.

Initial results indicate that we should be able to get good counting statistics and reliable analytical data from sea water samples of 20 to 30 liters for both the dissolved and particulate matter.

Briefly, the methods we have developed are as follows:

• Lead-210 activity is determined by first separating its Po^{210} granddaughter from the sample and then measuring the Po^{210} activity that has grown over a period of 5-6 months. The radiochemical procedures are outlined in figure 1.

Samples of 20-30 l are drawn from 30 l P.V.C. Niskin bottles and filtered by pressure filtration through 0.5μ Nucleopore filters. The filtered water is collected in plastic containers and acidified, and stable lead carrier is added as soon as possible after collection. Storage times of several weeks should allow for equilibration of the carrier in the acidified sample. Schell et al. (1972) give evidence for the rapid equilibration of lead added to sea water.

Lead is extracted from sea water on a column of Chelex-100 at a pH of 7.6 and recovered by elution with 2N HCL. Recovery is quantitative (see also Riley and Taylor, 1968). A Po^{208} tracer is added at this

point, and polonium is then removed by spontaneous deposition on silver (Flynn, 1968). Quantitative deposition of polonium is achieved in 75 minutes at a pH of 2.0 and a temperature of 85-90°C. Plating is carried out in the presence of hydroxylamine to reduce traces of oxidizing substances such as ferric iron, which interfere with the deposition of polonium, and citrate is added to prevent co-deposition of lead and other metals. Efficiency of polonium removal is monitored by α -counting of the Po^{208} tracer. Overall recovery of lead is determined by removing a small aliquot for atomic absorption analysis. Samples are then stored for several months to allow growth of Po^{210} . Finally, an additional separation of polonium followed by γ -counting is performed. Data on lead recovery, Po^{208} tracer recovery and Po^{210} activity allow calculation of the Pb^{210} activity originally present in the sample. Samples of particulate matter are processed in a similar manner following hot acid digestion in the presence of stable lead carrier.

All α -counting is performed in an α -spectrometer utilizing silicon surface-barrier detectors and a multi-channel pulse-height analyzer.

Radiochemical blanks are measured by processing highly purified water or blank filters through the entire analytical procedure. An unavoidable source of contamination arises from any Pb^{210} that may be present in the lead carrier, but this quantity should be very small (Weller et al., 1965).

Figure 1. Outline of analytical procedure for Lead-210

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ANALYSIS OF STABLE LEAD IN SEA WATER

Introduction

As part of a program to use radiotracer Pb^{210} as a means for understanding oceanic mixing processes and the transport of marine lead, we require detailed knowledge of the concentration of stable lead throughout the water column and its partitioning between dissolved and particulate phases. An important question is whether or not stable and radioactive lead behave dissimilarly in solution due to significant differences in chemical speciation.

This report details our attempts to develop reliable procedures for stable lead analysis, in part by careful elimination of sources of contamination, but principally by introducing a new method involving mass spectrometry of volatile lead chelates. We have previously described the determination of picogram amounts of chromium in sea water by electron capture gas chromatography of fluorinated chromium β -diketonates (Spencer, 1972), and we now propose to make quantitative measurements of similar volatile chelates of lead using isotope dilution mass spectrometry. Such measurements have the intrinsic advantage of being absolute, since only a knowledge of the isotopic spike is required, and the errors involved are amenable to simple treatment.

Lead Concentrations in Sea Water

The distribution of stable lead in natural waters has received considerable attention in recent years. Lead concentrations in uncontaminated sea water are apparently quite low, averaging 0.02-0.04 $\mu\text{g/liter}$.

However, the input of stable lead to the marine environment as a result of the industrial activities of man has steadily increased and is now estimated to exceed that due to natural weathering processes (Tatsumoto and Patterson, 1963). As a consequence, lead is one of the few elements for which discernible perturbations in normal concentration levels in open ocean waters can be attributed to anthropogenic sources. Lead concentrations two orders of magnitude higher than natural levels are frequently observed in nearshore waters adjacent to heavily industrialized areas, and careful work on open ocean samples has revealed significantly elevated lead concentrations in surface waters (Chow and Patterson, 1966).

Unfortunately, few marine laboratories have developed reliable techniques for low level stable lead determinations, and much of the published data on Pb in sea water and marine organisms must be held in question. This fact was underscored in two recent interlaboratory calibrations (Brewer and Spencer, 1970; Patterson and Settle, 1972) in which well characterized low lead level Pacific sea water samples were analyzed by several laboratories using standard techniques. The result of these studies (tables 1, 2) revealed one to two order of magnitude discrepancies in the lead content of the samples, indicating that most laboratories have severe problems with gross contamination, calibration of standards, or combination of these and other effects. It is possible that these samples were inhomogeneous on a liter scale, but as discussed later in this report, we feel that such effects cannot explain the large discrepancies indicated by the intercalibrations.

Methodology

Previous work has shown that lead salts react with the perfluoro-alkanoylpivalylmethanes to form thermally stable and quite volatile chelates (Kowalski and Isenhour, 1969; Belcher et al., 1970). Of these, $\text{Pb}(\text{fod})_2$, (Hfod = 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedione), is the most volatile, with a melting point of 74°C and a sublimation temperature of 62-63°C. In addition, this compound is stable up to 300°C and is therefore quite suitable for mass spectrometry. We have examined the mass fragmentation pattern of $\text{Pb}(\text{fod})_2$, which is given in table 3. A high proportion of the total ions are represented by relatively few major fragments such that analytical detection limits are enhanced.

Although we have found that $\text{Pb}(\text{fod})_2$ is readily extracted into hexane from aqueous solution at pH 8, it is not possible to extract Pb directly from sea water due to formation of large amounts of soap-like complexes of Hfod with alkali metals. Our approach is therefore to perform a preliminary dithizone extraction, followed by chelation of the Pb with Hfod and mass spectrometric measurement of the Pb-208/Pb-204 ratio for the $\text{Pb}(\text{fod})^+$ fragment. A detailed description of the procedure is given below. In addition, we report our experience with a heated graphite furnace atomic absorption technique modified from that of Duce (1973), which seems to produce reliable numbers if sources of contamination are stringently controlled.

Reagents - The following reagents are used in the lead extraction procedure and are subjected to extensive purification as noted:

Distilled water	Distilled, deionized water followed by double distillation in a two-stage quartz still.
HCl	Ultrex, J.T. Baker; certified less than 1 ppb Pb.
NH ₄ OH	Suprapur, E.M. Laboratories; certified 1 ppb Pb.
HNO ₃	Ultrex, certified 2 ppb Pb.
CHCl ₃	Mallinckrodt AR; redistilled in Pyrex.
H ₂ Dz	0.0015% in CHCl ₃ ; pre-purified by extraction in dilute ammonia followed by reacidification and extraction into fresh CHCl ₃ .
Hfod (Heptafluorodimethyl octanedions)	Peninsular Chemresearch; redistilled in Ultrex, 0.10 M in hexane.
NH ₄ Acetate	0.50 M; pre-purified by H ₂ Dz/CHCl ₃ extraction at pH 8.2.

Laboratory Operations - All labware, containers, separatory funnels, pipettes, etc. are FEP Teflon, polyethylene, or polypropylene. These items are cleaned repeatedly by soaking with AR HNO₃ (hot where possible), followed by soaking and rinsing with quartz double-distilled water. The cleaned items are then protected in polyethylene plastic coverings while in use. Most operations are carried out on an open laboratory bench, using extreme caution to avoid contact with unclean surfaces. Evaporations are performed in a fume hood under a protective glass shield.

Solvent Extraction - An 800 gram portion of the sample is weighed directly into a 1000 ml FEP Teflon separatory funnel and is acidified to pH 1.8 with concentrated HCl. A known amount (200-1000 ng) of an enriched Pb-204 tracer (94.20% Pb-204) is added using a polypropylene pipette. The sample is shaken thoroughly and then allowed to stand for one hour to equilibrate the tracer. The pH is readjusted to pH 8, using concentrated

NH_4OH , and the sample is then extracted for five minutes with 50 ml of 0.0015% $\text{H}_2\text{Dz}/\text{CHCl}_3$ solution. After phase separation, the chloroform layer is drained into a 125 ml separatory funnel (Teflon FEP) and back-extracted with 15 ml of 0.1 N HNO_3 . The acid extract is washed with a 15 ml portion of CHCl_3 , drained into a 30 ml Teflon FEP bottle and evaporated to dryness on a hot plate. The residue is taken up in 5 ml ammonium acetate buffer, and 5 ml of 0.1 M $\text{Hfod}/\text{hexane}$ is added. The bottle is tightly capped and heated at 60°C for several hours to allow formation of $\text{Pb}(\text{fod})_2$. For samples to be analyzed using the heated graphite furnace, the sample aliquot is reduced to 200 μl , and the tracer spike is omitted. Reagent amounts are likewise scaled down to give a final 1 ml acid extract. Although the initial acidification step could be omitted for the atomic absorption procedure, lead is easily lost to container surfaces at pH 8, and samples therefore are normally stored in an acid state.

Mass Spectrometric Isotope Measurements - A Finnigan 1015C combination gas chromatograph-low resolution quadrupole mass spectrometer is used for isotope ratio measurements. Initial efforts to chromatograph trace quantities of $\text{Pb}(\text{fod})_2$ were unsuccessful due to strong absorption effects, and samples are now introduced using a direct insertion probe. Approximately 50 μl of the $\text{Hfod}/\text{hexane}$ extract are evaporated onto a clean glass capillary probe tip. The probe is then placed in the insertion lock, and any excess reagent is pumped away before admitting the sample to the source.

Using a computed programmed voltage scan, the ion currents at AMU 499

($^{204}\text{Pbfod}^+$) and AMU 503 ($^{208}\text{Pbfod}^+$) are integrated during alternate 100 millisecond time segments as the lead chelate evaporates from the probe into the source. Scan times with the quadrupole instrument are chosen to be sufficiently short in order to eliminate significant error due to changing sample pressure in the source. In addition, each 100 ms scan segment is carried out in ten 0.1 AMU steps of 10 ms duration to compensate for possible shifts in the focusing of the quadrupole filter. The integrated ion currents are corrected for background noise and their ratios calculated. These ratios are then corrected for the known abundances of ^2H , ^{13}C , ^{17}O , and ^{18}O and averaged before computation of the lead content of the original sample.

Atomic Absorption Measurements - A Perkin-Elmer Model 403 spectrophotometer equipped with a HGA-70 Heated Graphite Atomizer was used for atomic absorption measurements. Using an Eppendorf pipette with a polyethylene delivery tip, 100 μl samples of the 0.1 N HNO_3 were injected into a pre-conditioned graphite tube. The programmer was set for a 60 second drying step at 100°C , a 60 second ashing step at 475°C , and a 20 second atomization step at 2000°C . Absorbance values were compared with calibration curves prepared using Pb standards in an identical matrix.

Preliminary Results

Contamination Levels - In order to make a reliable estimate of our total chemical and procedural blank, we have performed analyses using both isotope dilution and atomic absorption on aliquots of an ultra-high purity quartz-distilled water sample (Q-water) prepared by Dr. C. C. Patterson of the California Institute of Technology. This water is

certified to contain less than 1 ng Pb per kilogram. As such, it essentially provides a measure of our total chemical blank and all other sources of contamination. In addition, we have analyzed our own doubly quartz-distilled water for chemical blanks. The results of these analyses are summarized in Table 4.

Despite the fact that our chemical extraction procedures are carried out in an open laboratory, we have been able to achieve remarkably low levels of Pb contamination. These levels appear to average 15 ± 5 ng on a kilogram sample basis. In the isotope dilution procedure, a significant percentage of the blank is now known to arise from an interference from a minor fragment of $\text{Al}(\text{fod})_3$. The major source of the aluminum appears to be the acetate buffer and possibly the Hfod itself. Both reagents can be purified by extraction procedures, and apparent blank levels should be significantly lowered. An additional decrease could undoubtedly be achieved by instituting clean room procedures in a controlled environment.

Seawater Analyses - The accuracy of the isotope dilution procedure has been checked tentatively by pre-extracting duplicate samples of Woods Hole dockwater and spiking these with known amounts of common lead (Table 5). In general, the agreement is quite satisfactory, although the large uncertainty in the 25 ng/kg samples reflects the relatively large blank correction required. Ultimately, the technique will be checked against mass spectrometric isotope dilution measurements made by the CalTech lab, and we have recently agreed to participate in a seawater lead intercalibration study sponsored by I.D.O.E. and coordinated by C. C. Patterson of CalTech.

Although we have not yet initiated a large scale sampling program for stable lead measurements, we have determined the lead content of various seawater samples stored in our laboratory, and we include these as preliminary results in Table 5. These results appear to reflect severe problems in the sampling, handling, and storage of seawater lead samples. Both methods, for example, show tremendous quantities of lead in the Hudson 70 sample. Since this water is from the deep South Atlantic (below 1000 meters), it was expected to contain extremely low amounts of lead, and the observed values can only be ascribed to gross contamination during sampling.

In an attempt to determine whether the lead results reported in the Brewer-Spencer intercalibration (Table 1) might be real, we analyzed two of their original aliquots (1-76 and 1-100). These represent sub-portions of a large volume of unfiltered, acidified Pacific deep water, and as such, might also be expected to contain very minute amounts of lead. The first aliquot showed ≤ 5 ng/kg; the second contained 200 ng/kg. Since the errors in our analysis are reasonably well defined, we believe this discrepancy reflects a real variation in the sub-samples used in this study, again due to contamination during sample handling. At the same time, our results are very much lower than any of those reported in Table 1, and it seems improbable that the degree of inhomogeneity is as large as Table 1 indicates.

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TABLE 1

Lead Analyses from Trace Element Intercalibration Study of Brewer and Spencer (1970).

<u>Lab</u>	<u>Aliquot</u>	<u>Elapsed time (days)</u>	<u>Result ($\mu\text{gPb/kg}$)</u>	<u>Method</u>
1600/11/07	1-56	85	1.8	Solvent extraction APDC-MIBK atomic absorption
1443/17/07	1-9	86	0.46	Direct with anodic stripping voltametry
	1-81	103	0.45	
	1-97	107	0.42	
18/9/70	1-17	not reported	14.1	Adsorption with Chelex-100 eluted with HNO_3 ; atomic absorption in isopropanol solution
	1-23	"	6.1	
	1-98	"	10.9	

TABLE 2

IDOE Lead Intercalibration Study (Patterson, 1972)

<u>Laboratory</u>	<u>Sample size (g)</u>	<u>Result ($\mu\text{gPb/kg}$)</u>	<u>Method</u>
1	10	1.300	Anodic stripping voltammetry
2	500	.050	Atomic absorption; APDC-MIBK extraction
3	1200	.060	Atomic absorption; graphite furnace
4	15	.600	Anodic stripping
5	700	.055	Atomic absorption; carbon furnace
6	90	.180	Anodic stripping
7	500	.120	Atomic absorption; APDC extraction; tantalum boat
CalTech	1000	.014	Isotope dilution mass spectrometry

TABLE 3

Major Fragments and Relative Intensities
in the Mass Spectrum of $\text{Pb}(\text{fod})_2$.

<u>Fragment</u>	<u>AMU</u>	<u>Relative Intensity</u>
$[\text{Pb}(\text{fod})_2]^+$	798	10
$[\text{Pb}(\text{fod})_2 - \text{C}(\text{CH}_3)_3]^+$	741	22
$[\text{Pb}(\text{fod})]^+$	503	100
No assignment	482	30
$[\text{Pb}(\text{fod}) - \text{C}(\text{CH}_3)_3]^+$	446	15

TABLE 4

<u>Date</u>	<u>Sample</u>	<u>Method</u>	<u>Total Blank (ng/kg)</u>
2/14/73	Q-water (CalTech)	Isotope dilution	17.0
5/2/73	"	Graphite furnace	21
5/4/73	"	"	20
5/4/73	"	"	9.5
2/20/73	Q-water (WHOI)	Isotope dilution	11.2
4/27/73	"	Graphite furnace	15

TABLE 5

Analyses of Pb in Various Seawater Samples

<u>Sample</u>	<u>Method</u>	<u>Common Lead Spike (ng/kg)</u>	<u>Measured Pb Concentration (ng/kg)</u>
Pre-extracted, spiked Woods Hole dockwater	Isotope dilution	25.0	31 ± 4
"	"	50.0	57.2 ± 3
"	"	100.0	94.5 ± 4
Hudson 70 "deepwater"	Isotope dilution	--	834 ± 14
"	Graphite furnace	--	785 ± 28
Brewer-Spencer Inter-calibration (1970) Sample 1-76	"	--	≤ 5
Brewer-Spencer Inter-calibration (1970) Sample 1-100	"	--	200 ± 15
L.A. surface sample (unacidified)	"	--	≤ 5
L.A. surface sample (acidified, 2 days)	"	--	86 ± 4
L.A. surface sample	"	--	116 ± 3

ADSORPTION OF TRACE METALS ONTO THE
HYDROUS MANGANESE DIOXIDE SURFACE

J. W. Murray

Introduction

As part of our program in particulate matter in the oceans and the role that it may play in scavenging metals from sea water, an extensive experimental study has been completed of the surface chemistry of hydrous manganese dioxide.

Though the evidence for adsorption of metal ions on manganese dioxide in the marine environment is abundant, the hypothesis has yet to be adequately tested. We lack both a qualitative understanding of the mechanism of adsorption (i.e. the types of reactions that take place on the surface) and a quantitative means of predicting how much adsorption can take place. Those few models proposed to explain this process (e.g. Goldberg, 1954; Goldberg and Arrhenius, 1958) have been based on little or no experimental evidence and do not adequately explain many of the important observations.

The experiments summarized in this report were performed using a synthetically prepared hydrous manganese dioxide that was similar structurally (broad X-ray diffraction peaks centered at $7.4\text{\AA}$, $2.43\text{\AA}$ and $1.63\text{\AA}$) and in oxidation grade ($\text{MnO}_{1.93}$) to manganese phases found in nature. It is referred to here as δMnO_2 rather than $7\text{\AA}$ manganite because of controversy in the literature (Brown, 1971) regarding the existence of $7\text{\AA}$ manganite.

This report summarizes the results of experiments that close some of the gaps in our understanding of the adsorption mechanism and can be used to provide quantitative estimates of the metal enrichment in natural manganese deposits.

Electrostatic Aspects

The surface charge of δMnO_2 is pH dependent and the pH of zero point of charge, $\text{pH}(\text{ZPC})$ is located at pH 2.25. This means that for pH values greater than 2.25, the surface of δMnO_2 has a negative charge. Electrophoresis measurements indicate that the surface charge is a function of pH and that variation of the concentration of NaCl has little effect on the mobility of the particles. Thus H^+ and OH^- are the potential determining ions for the surface of δMnO_2 , which behaves like a weak acid in solution. Surface metal hydroxide groups participate in amphoteric acid-base reactions to produce a positively or negatively charged surface.

Though equation 1 is written as a dissociation reaction, one cannot distinguish by conventional analytical means between dissociation of protons from the surface or the binding or sorption of OH^- ions from solution.

Using alkalimetric titration curves to obtain the amount of strong base consumed by the surface, surface charge values were cal-

culated that approached $-100 \mu\text{coul}/\text{cm}^2$ at pH 8.0 in 0.01M NaCl. This would be equivalent to an adsorption capacity of $1 \times 10^{-5} \text{ eq}/\text{m}^2$ or $5 \times 10^{-6} \text{ moles}/\text{m}^2$ of divalent cations. Using the surface area of $260 \text{ m}^2/\text{g}$, this electrostatic adsorption capacity can be expressed in the same units used to express the ion exchange capacity of clays (meq/100g). The ion exchange capacity of δMnO_2 is compared with kaolinite and montmorillonite in Table 1.

TABLE 1

<u>Material</u>	<u>Ion Exchange Capacity</u>
Kaolinite	5-15 meq/100g
Montmorillonite	50-150 meq/100g
δMnO_2	250 meq/100 g at pH 8.0

This large negative charge produced by the acid-base properties of the surface only explains in part the high adsorption capacity of δMnO_2 . It cannot account for all the adsorption, as much higher adsorption densities (at least $1 \times 10^{-5} \text{ moles}/\text{m}^2$) were found for the transition metals.

Charge Density

The Gouy-Chapman Theory (see Stumm and Morgan 1970, p. 458) predicts that multivalent ions are concentrated in the double layer to a much larger extent than monovalent ions. On the basis of this theory,

it is frequently proposed (e.g. Goldberg, 1954; Goldberg and Arrhenius, 1958) that the degree of adsorption is a function of the charge density of the ions. However, this is apparently not reflected in the selectivity sequence that has been found for δMnO_2 . For example, Mg^{+2} has a higher ionic potential (charge to radius ratio) than Ba^{+2} but adsorbs much less. However, using the unhydrated radii to calculate charge density may be unrealistic because of the large energy of hydration of some ions. When hydrated radii are used to calculate ionic potential, Ba^{+2} has a larger value than Mg^{+2} and this might explain its greater adsorption. But, if charge density were the controlling factor, it would also be difficult to explain why Co^{+2} adsorbs much more strongly than Ni^{+2} . Both ions have similar radii and solution chemistry. There are obviously other controls on the adsorption of metal ions than simply coulombic attraction and charge density.

Specific Chemical Aspects

Goldberg (1954) suggested that if MnO_2 were negatively charged and iron oxide positively charged, the distribution of adsorbed ions between these two phases should indicate which elements are present in sea water as cations and which as anions. Those metals that exist in sea water as cations would adsorb on MnO_2 , and those as anions would adsorb on hydrous iron oxide.

Such a classification is complicated by the fact that adsorption can be due to more than electrostatic forces. For example, $\text{SO}_4^{=}$ and HPO_4^{-} are known to adsorb on negatively charged iron oxide surfaces (James, personal communication, and Hingston et al., 1967) and $\text{MnO}_4^{=}$ on negatively charged MnO_2 surfaces (Chan and Riley, 1966). Clearly, we cannot state that metals associated with MnO_2 exist as cations and that metals associated with iron oxide exist as anions in sea water.

The interaction of metal ions with metal oxides is best explained in terms of both chemical and coulombic attraction (Grahame, 1947; Stumm et al., 1970; James and Healy, 1972). The total standard free energy of adsorption, $\Delta \bar{G}^0$, is the sum of the total specific (chemical) adsorption energy, ϕ , and the electrochemical adsorption energy $ZF\psi$ (equation 2)

$$\Delta \bar{G}^0 = -\phi + ZF\psi \quad (2)$$

where ψ is the potential drop at the surface, F is the Faraday, and Z is the charge. Experimentally, it is very difficult to separate the energy of adsorption into its chemical and electrostatic components. Ionic species adsorbed in response to coulombic attraction alone obviously cannot adsorb in amounts greater than the number of equivalents necessary to neutralize the surface charge.

Experimental results from this work indicate that the alkali metal ions have no specific adsorption contribution, thus they only react electrostatically with the surface. No Na^+ or K^+ were found to adsorb on δMnO_2 below the $\text{pH}(\text{ZPC})$. As a group, the transition metal ions react more strongly with δMnO_2 than do the alkaline earths. Within each group there is a well defined selectivity sequence. Among the alkali earths, Ba interacts more strongly than Mg, and among the transition metals, Co interacts more strongly than Ni. The selectivity sequence for all of the metals studied is:

Those ions that are most easily adsorbed by increasing the pH are the most difficult to desorb by decreasing the pH. This is a reflection of the specific adsorption potentials that increase from the alkali earths to the transition metals.

Specific adsorption is thus the most likely explanation for the selectivity sequence. Unfortunately, the chemical processes controlling it are not well understood. Loganathan and Bureau (1973) maintain that during the adsorption process charge is conserved. When a metal ion is adsorbed, equivalent amounts of protons and structural cations are released. In their model of the surface, a metal ion that exhibits specific adsorption must penetrate into the structure of the δMnO_2 and replace structural Mn(II) or Mn(III). Our experiments have

demonstrated that this mechanism is much less important than suggested by Loganathan and Burau. In the most extreme case, only 10% of the cobalt adsorbed could be accounted for by manganese released to solution. Furthermore, electrophoresis experiments using Co(II) and Mn(II) demonstrated that charge was not conserved during adsorption. Thus, the most consistent explanation for specific adsorption on δMnO_2 is that it is a chemical reaction of the metal ions with the surface.

Alkalimetric titrations of δMnO_2 in the presence of metal ions indicated that the metal ions can penetrate in increasing amounts from Mg^{+2} to Co^{+2} into the compact part of the double layer to react with protonated sites on the δMnO_2 surface. Any ion that enters the compact layer can modify the double layer in such a way that the charge of the diffuse layer may become reversed. This reaction involves the replacement of a proton on the surface by a divalent metal ion on a one to one molar basis as shown by reaction 3.

It is possible that the metal ions are associated with more than one surface group. However, using a formation curve (a plot of ligand number versus the ligand concentration), Stumm et al. (1970) demonstrated that only monodentate associations ($\text{--}\overset{|}{\underset{|}{\text{MnO}}}\text{--Co}^+$) are formed. A similar reaction was found by Huang (1971) for metals interacting with $\gamma\text{-Al}_2\text{O}_3$.

Thus, the experimental evidence suggests we can explain the adsorption process as a combination of electrostatic attraction and specific adsorption. On the basis of its surface charge alone, δMnO_2 is an exceptional adsorbent. It has almost twice the electrostatic adsorption capacity of the most surface active clay minerals (Table 1). This adsorption is enhanced greatly for some minerals by specific adsorption.

A Quantitative Evaluation of the Adsorption Mechanism

An important aspect of this experimental study was to provide a quantitative evaluation of how much metal enrichment can be accounted for by adsorption. Clearly, these calculations will neglect the effect of factors such as organic complexing and other phases present that may also remove metals from sea water by adsorption. However, these calculations will provide an estimate of how effective the adsorption of uncomplexed metals by δMnO_2 is as a removal mechanism.

Bearing in mind the problems of extrapolation, the experimental results can be used to explain the observed metal distributions in the suspended matter of the Black Sea.

Spencer et al. (1972) observed a correlation between Co and Mn in the suspended matter of the Black Sea, and they suggested that this correlation is due to the adsorption of Co by δMnO_2 that is precipitated just above the oxygen zero boundary. Values for ad-

sorption density as a function of pH for cobalt concentrations from 10^{-3} to 10^{-8} M have been determined. A separate experiment showed that the adsorption density was independent of the amount of solid δMnO_2 for solid concentrations that approach the maximum amount of particulate Mn found in the Black Sea. An adsorption isotherm, adsorption density as a function of equilibrium cobalt concentration, is plotted in Figure 1 for pH 8. With increasing cobalt in solution, the amount adsorbed increases until monolayer saturation is reached at 1×10^{-5} moles/m². The data for this figure were obtained in 0.1M NaCl; thus, for applications to sea water, a correction factor must be applied because of the competitive effect of Na, Ca and Mg. At 1×10^{-8} M Co, this correction factor is approximately 50%, and it decreases to zero at 5×10^{-6} M. The corrected relationship for artificial sea water is given in Figure 1. The precision of these curves as determined by triplicate analyses at 1×10^{-8} M and 5×10^{-6} M is $\pm 25\%$.

We can now use these experimental data to compare with actual observations from Station 1449 from cruise 49 of the R/V ATLANTIS II in the Black Sea. The dissolved cobalt values were reported in Spencer and Brewer (1971) and the particulate values in Spencer et al. (1972).

Figure 2 shows the suspended Mn concentration, the total suspended matter concentration, and the observed ratio of cobalt to manganese in the suspended matter. The expected ratio of particulate Co to Mn can

Figure 1

Figure 2

be calculated using the experimental data in Figure 1. The adsorption density was converted to grams of cobalt adsorbed per gram of Mn (as δMnO_2) assuming a surface area of $260\text{m}^2/\text{g}$. This was the experimentally measured surface area for the δMnO_2 used in these experiments. The experimentally predicted ratio of particulate Co to Mn is shown in Figure 2.

The predicted ratio agrees well with the observed ratio at the point corresponding to high suspended Mn concentrations; however, it is much lower than the observed ratios at low Mn concentrations. At depths above and below the particulate Mn maximum, both Mn and Co concentrations are low. It is conceivable that this anomaly between the experimentally predicted and the observed value is influenced by the contribution of Co and Mn in detrital phases.

The hypothesis proposed by Spencer et al. (1972) that the correlation between particulate Co and Mn is due to adsorption of Co by MnO_2 appears substantiated by the experimental evidence in spite of the assumptions in comparing the experimental data with the field data. These assumptions are that the surface area of the experimental MnO_2 and the particulate Mn in the Black Sea are similar, that the mineralogy of the phases is similar, and that cobalt is incorporated only by surface adsorption and that no Co is included in growing MnO_2 particles. The coefficient of variation of the dissolved cobalt measurements is $\pm 15\%$. No estimate was given for the coefficient of

variation for the particulate Co. Thus, considering the errors in extrapolation and the errors in the analytical measurements, the agreement between the observed and predicted particulate Co values is quite good.

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CARBON, NITROGEN AND PHOSPHORUS
IN THE BLACK SEA

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ABSTRACT

We have used hydrographic and nutrient data from Cruise #49 of the R.V. Atlantis II to the Black Sea to derive a model for the flux of carbon, nitrogen and phosphorus through the oxygen-sulfide interface that exists between 125 and 250m below the surface. Breaks in the potential temperature-salinity diagram indicate that this region is a linear mixing interval of some 250 meters between the cold winter water above and the warmer, more saline, inflow water beneath. A one dimensional advection-diffusion model between these boundaries allows us to calculate the ratio of the vertical eddy diffusion coefficient to the vertical advective velocity as being 0.09 km. Fitting the vertical profiles of total carbon dioxide, ammonia and phosphate to this model, we observe consumption rates (J) of all three species ($J_{\text{CO}_2} = -1 \times 10^{-6} \text{ mole kg}^{-1} \text{ year}^{-1}$, $J_{\text{NH}_3} = -0.1 \times 10^{-6} \text{ mole kg}^{-1} \text{ year}^{-1}$ and $J_{\text{PO}_4} = -0.01 \times 10^{-6} \text{ mole kg}^{-1} \text{ year}^{-1}$). These consumption rates are in contrast to the production rates inferred from the stoichiometric oxidation model. The consumption rate is in fact a net value representing the difference between chemosynthetic consumption and respiratory production of carbon dioxide by bacteria living at the oxygen-sulfide interface, and similar arguments hold true for ammonia and phosphate.

Experimental measurements of chemosynthetic rate by dark uptake of ^{14}C -bicarbonate yield a value of 36 moles C meter $^{-2}$ year $^{-1}$. We suggest that this is too high and attempt to set an upper limit for the true value by calculating βE , the redox buffer capacity of the deep water, and transporting this upwards. From this we can calculate various carbon dioxide fixation rates depending upon the metabolic uses to which the oxidizable equivalents are put. The formation of glucose at 50% efficiency would give a carbon dioxide fixation rate of 1.50 moles meter $^{-2}$ year $^{-1}$. A disturbing

feature of the proposed model is that oxidation of sulfide appears to take place in the absence of oxygen.

Introduction

Anoxic basins, though forming only a trivial percentage of the world ocean by volume, are none the less widely regarded as important chemical oceanographic phenomena. In these basins the consumption of abyssal oxygen by the bacterial degradation of organic matter, which occurs universally in the oceans, is taken to extremes. As dissolved oxygen vanishes, the bacteria turn to other terminal electron acceptors to oxidize organic matter, and first nitrate and nitrite, then sulphate are reduced (Richards 1965). The reduction of sulfate to sulfide has important consequences: the system becomes toxic to most life forms, the redox potential of the system is abruptly lowered, and many chemical species (e.g. Fe^{3+} , Mn^{4+}) are transformed to their reduced states.

The study of abyssal oxygen consumption has been of considerable historical interest (Riley 1965) and is still the topic of active controversy today (Craig 1971, Menzel and Ryther 1968). We know that mixing processes replenish deep water, and the normal oceanic steady state is such that dissolved oxygen is not fully consumed. Riley (1951) and Wyrski (1962) have examined the effects of oceanic mixing on the oxygen minimum, and their conclusions are now generally accepted. Such mixing models have not been applied to anoxic basins, though it has been shown (Richards 1965) that vertical density stratification and long deep water residence times are characteristic of these systems. Examples of anoxic basins are the Black Sea, the Cariaco Trench and many fjords. In this paper we apply a simple one dimensional vertical advection-diffusion model to describe the mixing and the flux of the nutrient elements, oxygen and carbon dioxide through

an anoxic basin (the Black Sea) together with estimates of primary production at the surface and chemoautotrophic production at the oxygen-sulfide interface.

The data are taken from Cruise 49 of the R/V ATLANTIS II to the Black Sea in March and April of 1969 (Brewer 1971) and are available on request.

Collection and Analysis of the Samples

Samples were collected in Teflon lined brass Nansen bottles for most analyses. At a few stations in the earlier part of the cruise (Stations 1430-1435), casts were made with non-metallic bottles which were soon discarded due to mechanical unreliability. The sulfide values recorded from these bottles were generally slightly higher than those from the Nansen bottles, and there remains the possibility that some chemical reaction took place between the Nansen bottle and the sample (Park 1968). Samples were drawn from the Nansen bottles for analysis immediately upon collection. At each station, a continuously recording oxygen probe was lowered to define the boundary between the oxic-anoxic water, and bottles were placed with the aid of this information.

Oxygen was determined by Winkler titration (Carpenter 1965). Sulfide samples were fixed with a zinc chloride solution prior to analysis and determined by a methylene blue method (Grasshoff and Chan 1969). Dissolved phosphate, silicate, nitrate, nitrite and ammonia were measured colorimetrically by the six channel Technicon Autoanalyzer System described by Grasshoff (1969). Briefly, phosphate was determined by a molybdenum blue method using ascorbic acid reduction. Silicate was also determined with

a molybdenum blue method using a metol sulfite reduction and oxalic acid to suppress the phosphate interference. Nitrate was reduced to nitrite with a copper-cadium couple, and nitrite was determined with sulfanilamide and N-1-naphthylethylene diamine. Ammonia determinations were carried out by hypobromite oxidation of the ammonia to bromoamine and successive reaction with starch iodide. An important point is that samples for nutrient analysis were bubbled with air to oxidize hydrogen sulfide prior to analysis. This may have resulted in some loss of ammonia (Fonselius, pers. comm.).

pH determinations were carried out by means of a glass electrode in a temperature controlled cell. The measurements were standardized using N.B.S. buffers and corrected to in situ pH according to Gieskes (1969). Alkalinity was determined by the standard acid addition technique of Anderson and Robinson (1946), and from the pH and alkalinity data, calculations of all CO_2 species were made. The data obtained for total carbon dioxide and alkalinity are most unusual, the concentration of total carbon dioxide having approximately twice the normal oceanic ratio to chlorinity and the alkalinity being 2.5 times higher. This is not totally unexpected since other workers (Skopintsev et al. , 1967) have found similar results but it would be desirable to check these data by independent means.

All nutrient and carbon dioxide data originate from Dr. K. Grasshoff, of the Institut für Meereskunde, Kiel, and have been compiled, together with the hydrographic data by Brewer (1971). We do not wish to give

a lengthy description of analytical procedures or precision since these were not directly under our control. Few samples were analyzed in duplicate and inspection of the data for ammonia and phosphate suggests that the precision can have been no better than $\pm 10\%$ due to the analytical difficulties created by the anoxic conditions. Nevertheless, we believe these data to be the best available and we specifically wish to thank K. Grasshoff, S. Fonselius and R. Sen Gupta for their generosity in making their results available.

Primary and chemosynthetic productivity measurements were made by Sen Gupta and Jannasch (1973). The samples were taken with Nansen bottles and were incubated at various light intensities at $17^{\circ} \pm 1^{\circ}\text{C}$ after the addition of $1 \mu\text{C ml}^{-1} \text{ }^{14}\text{C}$ -bicarbonate. After incubation, the samples were poisoned, filtered and stored for counting ashore several months later. Samples for the determination of chemosynthetic activity were taken with sterile Niskin samplers, transferred to dark glass bottles, injected with $50 \mu\text{C ml}^{-1} \text{ }^{14}\text{C}$ -bicarbonate, incubated, filtered and stored as were the primary productivity samples.

Nutrients in the Black Sea

Previous Data

Caspers (1957) has provided an excellent review of the early hydrochemical data on the Black Sea. Although the information is somewhat sparse, he concluded that the Black Sea contained maximum quantities of phosphorus of $632 \text{ mg P}_2\text{O}_5 \text{ l}^{-1}$ at 2000 m, $1.26 \text{ mg NH}_3 \text{ l}^{-1}$ at 2000 m and $0.015 \text{ mg NO}_3 \text{ l}^{-1}$ at 150 m. Oxygen was found to be depleted to zero concentration at depths of between 125 m and 300 m and a maximum concentration of hydrogen sulfide of $5.8 \text{ cm}^3 \text{ l}^{-1}$ at a depth of 2000 m was reported.

As analytical methods have improved and more chemists have turned their attention to these problems, these data have improved significantly. Fonselius (1973) has reviewed the data on phosphate distribution up to the present day and has described a box model of phosphorus in the Black Sea. Using the data available to us in this paper, he concluded that in order to preserve a steady state some 6.7×10^3 tons of phosphorus must accumulate in the sediments each year. Given a sediment surface area below the anoxic zone of $3.7 \times 10^5 \text{ km}^2$, this implies a phosphorus accumulation rate of $1.8 \times 10^{-2} \text{ grams m}^{-2} \text{ yr}^{-1}$. He also notes that very little phosphorus is found in the bottom sediments, and this is difficult to reconcile with the model.

Sen Gupta (1969, 1971) has discussed the nitrogen cycle in anoxic basins and examined the data with respect to redox equilibria. His values of pE calculated using various couples of the nitrogen system, indicate that the $\text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^{++}$ system is not in equilibrium in the deep anoxic water. His treatment of the data may be in error because of the assumption that all ammonia results from the reduction of nitrate and that none is released directly from decomposing organic matter (Reaction 4).

Skopintsev et al (1967) have examined the distribution of organic carbon, nitrogen and phosphorus and have provided analytical data that are in fair agreement with those we use here.

Stoichiometric Oxidation Model

The most detailed model of the oxidative processes that lead to the accumulation of large amounts of phosphate, ammonia and carbon dioxide in anoxic basins is the stoichiometric oxidation model described by Redfield et al (1963) and Richards (1965). In this model, organic matter photosynthetically produced at the sea surface is schematically represented as $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$, thus combining C, N and P in the observed "Redfield ratios" of C:N:P = 106:16:1. On sinking of the organisms below the euphotic zone, bacterially mediated oxidative decomposition occurs releasing CO_2 , NO_3^{-2} and PO_4^{-3} to the sea water as in (1).

When nearly all of the dissolved oxygen has been consumed in this way, the bacteria turn to nitrate ions as the terminal electron acceptor necessary to continue to oxidative process. This denitrification can be represented as

In addition, there is the possibility that some of the ammonia thus generated is oxidized to nitrogen.

Finally, when all nitrate and nitrite have been consumed, sulfate reduction occurs with the resultant production of sulfide.

The ammonia formed in this step is almost certainly not oxidized.

The model is an attempt to predict the steady state concentrations of C, N, P, O and S in anoxic systems and to write formalized chemical equations to describe the processes which lead to the steady state. However, certain deficiencies are inherent in this approach; it takes no account of oceanic mixing or of the rates at which the system is driven to the steady state; moreover, the reactions may take place in the water column or in the sediment, and the products then transported to the site of the observation, the site of the reaction remaining undefined.

Deuser (1970) has examined the evidence for the origin of hydrogen sulfide in the Black Sea and has concluded that >90% of the sulfide does indeed come from the reduction of sulfate and not from organic sulfur compounds, and that the principal site of sulfide production is at the sediment-water interface.

Hydrographic Characteristics of the Black Sea

The Black Sea is an almost completely isolated basin; connected to the world ocean by the Bosphorous, with a maximum sill depth of only 34 m (Gunnerson and Ozturgut 1972), and the Dardanelles. Through this narrow connection, water exchange with the Mediterranean Sea occurs, the more saline Mediterranean water creating a deep inflow into the Black Sea and the less saline Black Sea water forming a surface outflow. The inflow

to the Black Sea may be discontinuous depending on seasonal conditions (Bogdanova 1961), and estimates of the volume vary from $328 \text{ km}^3 \text{ yr}^{-1}$ (Merz and Moller 1928) to vanishingly small (Ulliyot and Igaz 1946). Merz and Moller (1928) give the salinity of the inflowing water to be $33\text{--}35^\circ/\text{oo}$. This water rapidly sinks and mixes with Black Sea water and spreads out over the basin. Ostlund (1969, 1973) has shown on the basis of ^{14}C data that this water, between approximately 300 m and 1700 m, has a residence time of about 1000 years; this corresponds to the linear θ -S region in Figure 1 between $21.8^\circ/\text{oo}$ and $22.2^\circ/\text{oo}$. Below this, the deeper water is considerably older and is probably renewed only by eddy diffusion.

The two gyre circulation pattern of the Black Sea is such that the isophcnals slope upwards towards the center of each basin (Neumann 1944). The stability maximum of the water column occurs at a σ_θ level of approximately 16.0, and some 40-50 m below this, at a σ_θ level of 16.41, the characteristic transition from an oxidizing to a reducing environment occurs with appearance of sulfide. The depth of this transition varies from 250 m below the surface around the perimeter of the basin to only 100 m near the center of each gyre. Spencer and Brewer (1971) have shown that data from different stations may be superimposed on the same profile with zero depth arbitrarily set at a constant density level, most conveniently for chemical purposes the oxygen-sulfide boundary.

Vertical Advection-Diffusion Model

The use and limitations of the application of the general equation for advection and diffusion of chemical species within the ocean in the vertical dimension alone is well documented in the literature (Wyrтки 1962, Munk 1966, Craig 1969), and no detailed discussion is necessary here. For

2

a non-radioactive species, the general equation reduces to

$$(5) \quad K \frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} + J = 0$$

for the steady state condition, where K is the vertical eddy diffusion coefficient, ω is the vertical advective velocity, and J is the rate of production or consumption of the chemical species of mass fraction C , equal to zero for conservative tracers such as temperature or salinity. The solution is derived in terms of K/ω , or Z^* in the notation of Craig (1969), for a conservative tracer and in terms of Z^* and J/ω for a non-conservative tracer with J constant with depth. Wyrski (1962) observed that an exponential variation of J with depth fitted the observed oxygen distribution in many parts of the ocean and in this case equation (5) then becomes

$$(6) \quad K \frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} + J_0 e^{-\mu z} = 0$$

with a two parameter solution in terms of J_0/ω and μ (Craig and Weiss 1970). The model is applicable over linear regions of the θ - S diagram where horizontal velocities and concentration gradients are small.

In Figure 1, the region from $S^0/\text{‰} = 19.6^0/\text{‰}$ to $21.7^0/\text{‰}$ is linear and represents a mixing interval of some 200m to 250m in depth between the horizontally advecting core of inflowing deep water and the colder surface water formed in winter. Spencer and Brewer (1971) have fit the temperature and salinity data over this interval with the parameter Z^* , and have given an average value of $Z^* = 0.09$ km as characterizing the interval over the

entire Black Sea. Using a best estimate for the Bosphorous inflow of $190 \text{ km}^3 \text{ year}^{-1}$ and assuming this to advect uniformly over the surface of the mixing interval, they calculated a vertical advective velocity of 0.5 m year^{-1} and a vertical eddy diffusion coefficient of $44 \text{ m}^2 \text{ year}^{-1}$, or $0.014 \text{ cm}^2 \text{ sec}^{-1}$. (An unfortunate printing mistake in Spencer and Brewer (1971) gave $K = 0.14 \text{ cm}^2 \text{ sec}^{-1}$; the correct value is unusually low being only 10 times the molecular diffusion coefficient for heat, and 10 times less than the generally allowed lower limit for eddy diffusion in the oceans (Munk 1966). The physical reality of these parametric values has often been questioned, and the low apparent value may be the result of the high degree of stability of the water column in which case the assumption of an eddy diffusion coefficient constant with the depth may be in doubt.) We shall use these estimates of K and ω in our subsequent calculations.

Finally, in order to get a simple estimate of the upward transport of a chemical species from its observed profile through the mixing interval, we shall write

$$(7) \text{ Flux} = K \frac{\partial C}{\partial z} + \omega C$$

Carbon Dioxide, Ammonia and Phosphate

Figure 2 shows vertical profiles of total carbon dioxide, ammonia and phosphate at station 1466 in the deepest part of the eastern basin of the Black Sea, and the depth of the oxygen zero level is indicated at a depth of 125 m. At this station the mixing interval studied by Spencer and Brewer (1971) lies between the depths of 50 and 225 m. Each profile shows a characteristic shape over this region, the carbon dioxide profile being concave throughout,

the ammonia profile showing a sharp increase at the oxygen zero level with an almost linear increase to 700 m, and the phosphate profile showing a sharp increase above oxygen zero with a reversed cusp at the boundary and a minimum at about 220m, then increasing into the deep water.

In order to characterize the general situation, we have fit data from several stations on to a single composite profile. Figure 3 shows such a plot for total carbon dioxide. We have fit this data with the solution of equation (5), for a stable non-conservative component. The least squares fit gave $J/\omega = -2.107 \pm .026 \times 10^{-3} \text{ moles kg}^{-1} \text{ km}^{-1}$ and J is thus equal to $-1.05 \times 10^{-6} \text{ moles kg}^{-1} \text{ yr}^{-1}$. Carbon dioxide is not being produced within this mixing interval; it is being consumed.

A similar composite plot for ammonia is shown in Figure 4. The analytical scatter is greater than that for carbon dioxide, and the profile is not monotonic; biochemical reactions and redox equilibria perturb the profile at the oxygen zero level and set an upper boundary for the system other than that imposed by temperature and salinity. We have fit the ammonia profile with a constant J term from the lower θ - S boundary to the oxygen zero level. This shifting of boundary conditions is open to criticism; however, theoretically once Z^* for a mixing interval has been established, all sub-divisions within that interval should be characterized by the same parametric value. We have tested this by fitting Z^* for composite temperature and salinity data over the more restricted range required by the ammonia profile and found it to be true.. The value of J/ω for ammonia derived in this way is $-200 \times 10^{-6} \text{ moles kg}^{-1} \text{ km}^{-1}$, and J is thus equal to $-0.1 \times 10^{-6} \text{ moles kg}^{-1} \text{ yr}^{-1}$. Again, within this interval, ammonia is being consumed.

The composite phosphate profile is shown in Figure 5. The large amount of scatter among the data points gives cause for concern, however, each individual station profile shows the same feature of a maximum followed by a sharp reversal. We have fit the profile by eye using the solution of equation (6), allowing for an in situ consumption which varies exponentially with depth, and the two parameter fit gave $J_0/\omega = -1 \times 10^{-6}$ moles kg^{-1} and $\mu = 30 \text{ km}^{-1}$. The boundary conditions were chosen as for ammonia. The consumption rate thus derived is given by

$$(8) J_0 = -5 \times 10^{-4} e^{-0.03z} \times 10^{-6} \text{ moles kg}^{-1} \text{ year}^{-1}$$

The median J is $.0086 \times 10^{-6} \text{ moles kg}^{-1} \text{ year}^{-1}$ and occurs at a depth of 80 meters below oxygen zero.

In calculating in situ consumption rates for carbon dioxide, ammonia and phosphate in this way, we are, of course, observing net changes, and the J calculated is a parameter of mixed functionality. Carbon, nitrogen and phosphorus are fixed in the photosynthetic zone and released from decomposing plankton at depth. This remineralization can be seen in the sharp increase in dissolved phosphate and the decrease in dissolved oxygen (Fig. 5&7) which begins 50-70 meters above oxygen zero. Carbon dioxide and ammonia must also be produced in this process. Phosphate is known to be released more rapidly from decaying organisms (Riley 1951, Grill and Richards 1964) than is carbon dioxide or ammonia, and these kinetic factors are partly responsible for the shapes of the profiles. However, within this mixing interval there exists a population of chemoautotrophic bacteria (Sorokin 1964, Sen Gupta and Jannasch 1973, Tuttle and Jannasch 1973, and we suggest that these bacteria are responsible for the observed net consumption of carbon dioxide.

We can write

$$(9) \quad J_{CO_2} \text{ (net)} = J_{CO_2} \text{ (respiration)} - J_{CO_2} \text{ (fixation)}$$

and similarly for ammonia and phosphate. It is interesting to calculate the ratio of the net consumption rates observed

$$(10) \quad J_{CO_2} : J_{NH_3} : J_{PO_4} = 116 : 11 : 1.0$$

The Redfield ratios (Redfield 1934) commonly observed in oceanography (Equation 1) are 106 : 16 : 1; thus the mole ratios predicted by the stoichiometric oxidation model are preserved, but by a very different mechanism.

Chemosynthesis

In order to calculate absolute rates of carbon, nitrogen and phosphorus, uptake and regeneration within the mixing interval measurements of the chemosynthetic rate must be made. Chemosynthetic bacteria have been defined by Thimann (1963) as "those organisms that grow on carbon dioxide and water together with an oxidizable compound or element." Sorokin (1964) has made dark ^{14}C uptake measurements of chemosynthesis in much the same way as the data reported here. He found variable values with a maximum rate of up to $3 \times 10^{-3} \text{ g C meter}^{-3} \text{ hour}^{-1}$ in a thin layer at the oxygen sulfide boundary.

In Figure 6, we show the 34 measurements of chemosynthetic rate made by Sen Gupta at 13 stations (Sen Gupta and Jannasch 1973) drawn on a composite profile. A maximum rate was observed approximately 50 meters below oxygen zero of about $1.5 \text{ mg C meter}^{-3} \text{ hour}^{-1}$, and we can select an average value of $1 \text{ mg C meter}^{-3} \text{ hour}^{-1}$ as representing the observed chemosynthetic rate over a 50 meter depth interval. The average chemosynthetic rate measured is then

36 moles meter⁻² year⁻¹; a factor of three less than the maximum value measured by Sorokin. Deuser (1971) has suggested that the upper limit for chemosynthesis must be close to 1.2 moles meter⁻² year⁻¹; however, this is not a direct estimate but represents allowed errors in organic carbon mass balance calculations. In Table 1, we show the quantities of carbon, nitrogen and phosphorus which would have to be fixed (assuming C: N: P = 106: 16: 1) per square meter per year if Sen Gupta's values are correct, and these data are compared to the upward flux calculated from equation (7). In order to reconcile the two estimates, we should have to postulate that 95% of the carbon dioxide fixed each year be recycled within the mixing interval, and we would need energy to drive this cycle.

To set these data in perspective, it is necessary to state some fundamental points. In order to synthesize protoplasm from simple inorganic compounds, we need energy. Energy for the proposed chemosynthesis is derived from thermodynamic disequilibrium. Thermodynamic disequilibrium is promoted by the flux of organic matter which originates photosynthetically at the sea surface. Hence the energy available for chemosynthesis can be no greater than that transported by the flux of organic matter into the anoxic zone. Primary production in the Black Sea has been estimated at about 8.3 moles C meter⁻² year⁻¹ (Sorokin 1964, Sen Gupta and Jannasch 1973, Deuser 1971), and thus the claimed chemosynthetic rate of 36 moles C meter⁻² year⁻¹ appears to be too high. It is not our intention to decry the difficult experimental work carried out in attempts to obtain direct measurements of the chemosynthetic rate. The high values obtained could arise from a number of sources, such as heterotrophic uptake of carbon dioxide, surface reactions or leakage

of atmospheric oxygen into the sample during transfer, all of which are well known by the investigators. Since the experimental data appear to be inaccurate we must find some other estimate of chemosynthesis.

Redox Buffer Capacity of the Deep Water

We have attempted to set an upper limit on the chemosynthetic rate by calculating the upward flux of total reduced species. Non-photosynthetic organisms tend to restore equilibrium by catalytically decomposing thermodynamically unstable compounds through energy yielding redox reactions (Stumm and Morgan 1970). Bacteria are known which can oxidize the following chemical species (Thimann 1963):

Ammonia
Nitrite
Hydrogen gas
Carbon monoxide, formaldehyde, formate or methanol
Methane or other simple hydrocarbons
Ferrous and manganous salts
Hydrogen sulfide, sulfur or thiosulfate

We can sum these by considering the homogeneous pE buffer capacity, β_e , (Thorstenson 1970) of the water at the lower boundary:

$$(11) \quad \beta_e = \left(\frac{\partial C_{ox}}{\partial pE} \right)_{pH}$$

where $\bar{n}$ is the number equivalents of strong oxidizing agent added to the solution. The use of partial derivatives is necessary because of the differences in pH dependence for the various redox reactions.

$$(12) \quad \left(\frac{\partial C_{ox}}{\partial pE} \right)_{pH} = \left(-\bar{n} \frac{(\sum \text{equivalents of reduced species})}{\partial pE} \right)_{pH} = -\sum \bar{n}_i \left(\frac{\partial M_{xi}}{\partial pE} \right)_{pH}$$

where m is the number of moles of species x in the i^{th} redox reaction which has an n electron transfer. Thorstenson (1970) derived a value of β_e equal to 4.9×10^{-2} equivalents kg^{-1} for Black Sea deep water, and we follow a similar scheme here, incorporating extra terms for the manganous ion and the dissolved organic carbon. Dissolved organic carbon analyses have been reported by Deuser (1971), and we have arbitrarily selected 1% of the total dissolved organic carbon as representing a labile, oxidizable fraction. Then

$$(13) \quad \beta_e = 3 \left(\frac{\partial M_{\text{NH}_4^+}}{\partial pE} \right)_{\text{pH}} + 8 \left(\frac{\partial M_{\text{HS}^-}}{\partial pE} \right)_{\text{pH}} + 8 \left(\frac{\partial M_{\text{H}_2\text{S}}}{\partial pE} \right)_{\text{pH}} + 8 \left(\frac{\partial M_{\text{CH}_4}}{\partial pE} \right)_{\text{pH}} \\ + 4 \left(\frac{\partial M_{\text{org. C}}}{\partial pE} \right)_{\text{pH}} + 2 \left(\frac{\partial M_{\text{Mn}^{+2}}}{\partial pE} \right)_{\text{pH}} = 1.6 \times 10^{-2} \text{ equivalents } \text{kg}^{-1}.$$

In Table 2, we show the calculated β_e for each species. The total β_e is somewhat lower than that calculated for 1900 m depth by Thorstenson, and this is due to the lower quantities of reduced species present at the lower boundary of the linear mixing interval. It can be seen that more than 90% of the redox buffer capacity is due to the presence of sulfide.

In order to derive the upward flux of reduced equivalents, we shall consider β_e as a stable non-conservative tracer and transport it in accordance with the advection diffusion model. This is a difficult problem. β_e is a function of pH and hence is temperature, pressure and alkalinity dependent; moreover, physically mixing a complicated function has its conceptual difficulties. In fact, the pH change from the lower boundary of the mixing interval to the oxygen-sulfide boundary is +0.05 pH

units and will not perturb the calculation markedly. Applying (7), and assuming β decreases to a very small value 10m above the oxygen-sulfide boundary, we find an upward flux of 12.0 equivalents $\text{m}^{-2} \text{year}^{-1}$.

These oxidizable equivalents are available to chemosynthetic bacteria, and depending upon the metabolic used to which they are put, various CO_2 fixation rates can be calculated. As an example, we shall consider the formation of glucose:

and therefore

The transformation requires 24 electrons, and hence we calculate that carbon dioxide may be fixed at a rate of 3.0 moles $\text{m}^{-2} \text{year}^{-1}$. Assuming a 50% efficiency factor (McCarty 1964), we finally arrive at a rate of 1.5 moles $\text{m}^{-2} \text{year}^{-1}$.

From our calculation of J_{CO_2} , and considering a 250m mixing interval, we calculate an observed net consumption of 0.25 moles $\text{m}^{-2} \text{year}^{-1}$.

We suggest that this is derived from chemosynthetic consumption of 1.5 moles $\text{meter}^{-2} \text{year}^{-1}$ and respiratory production of 1.25 moles $\text{m}^{-2} \text{year}^{-1}$.

Our 50% efficiency factor is probably high, and unless there is a major upward flux of a reduced species unknown to us we suggest that this represents an upper limit for chemosynthetic activity. The rate is similar to that derived by Deuser (1971) and is close to the total upward flux of carbon dioxide (1.96 moles $\text{m}^{-2} \text{year}^{-1}$) given in Table 1.

Discussion

Fitting the observed profiles of total carbon dioxide, ammonia and phosphate across the oxygen-sulfide boundary of the Black Sea with a vertical advection-diffusion model, we derive net consumption rates of all three species. This consumption is probably due to chemosynthetic bacteria utilizing the upward transport of sulfide, ammonia, methane, and manganous ion and catalytically oxidizing these species. In order to sum these effects, we have calculated β_e , the redox buffer capacity of the water at the lower boundary and calculated the potential electron flux available in mixing of this water. The chemosynthetic rates calculated in this way (approximately 18% of surface primary productivity) are in contrast to the experimentally determined rates, being a factor of 20 lower.

In writing this paper, we set out to describe the nutrient relationships with a simple mixing model. The interpretation of the results has been unusually difficult. Totally inorganic removal mechanisms would, for instance, require precipitation of calcium carbonate, ferric phosphate and loss of ammonia to a solid phase or to gaseous nitrogen, all in the proportions of the Redfield model. We reject this, but find some disturbing features of the proposed mechanism. Using equation (7), we calculate a value of $75 \times 10^{-3} \text{ moles m}^{-2} \text{ year}^{-1}$ for the upward flux of sulfide. Similarly diffusing dissolved oxygen downwards against the upward advective gradient, we calculate a value of $3 \times 10^{-3} \text{ moles m}^{-2} \text{ year}^{-1}$.

The profiles are shown in Figure 7. Considering

we see that 69×10^{-3} moles $\text{m}^{-2} \text{year}^{-1}$ of sulfide remain to be oxidized by some other chemical species at present unknown. Moreover, the model shows significant uptake of carbon dioxide below the oxygen-sulfide boundary, indicating that sulfide may be oxidized in the total absence of dissolved oxygen. The data are not precise but would indicate a $J_{\text{H}_2\text{S}}$ of -0.4×10^{-6} mole $\text{kg}^{-1} \text{year}^{-1}$. As shown earlier $J_{\text{CO}_2} = -1.0 \times 10^{-6}$ moles $\text{kg}^{-1} \text{year}^{-1}$, thus consumption rates are roughly in agreement with reaction (16). Reaction (16), however, has a positive free energy ($\Delta G = +212 \text{ K cal/mole}$), thus energy must be supplied for it to proceed, and for chemosynthetic processes, this is normally provided by the presence of oxygen.

These results are of course strongly dependent on the assumptions of the one-dimensional model and suggest a complicated picture that would bear further investigation. We have not considered heterotrophic organisms in this model, and carbon dioxide uptake by heterotrophic bacteria remains a possibility (Jannasch, pers. comm.). Hydrogen sulfide may also be consumed by metal reduction and precipitation, but the amounts are too small to account for the effects we observe here. Finally, if the model we propose is real then the bacterial population at the interface would seem to act as a fairly effective "lid" on the anoxic basin, trapping much of the upward flux of carbon dioxide, ammonia and phosphate and returning it to the deep water in particulate form, perhaps forming one of the mechanisms whereby these basins act as "nutrient traps."

Acknowledgements

We wish to thank K. Grasshoff, S. Fonselius and R. Sen Gupta for permission to use their data, and H. Jannasch and J. Tuttle for many informative discussions. This work was supported by N.S.F. Grants GA-13574 and FA-11659, and AEC Contract No1 AT(11-1) -3566.

TABLE 1

UPWARD TRANSPORT OF CARBON DIOXIDE, AMMONIA AND PHOSPHATE CALCULATED
FROM EQUATION 7 AND COMPARED TO MEASURED CHEMOSYNTHETIC RATES

Element	Concentration (moles m ⁻³)	$\frac{dc}{dz}$ (moles m ⁻⁴)	Flux (moles m ⁻² yr ⁻¹)	Estimated Fixed (moles m ⁻² yr ⁻¹)
C	3.77	1.6×10^{-3}	1.96	36.2
N	21×10^{-3}	1.6×10^{-4}	22×10^{-3}	5.5
P	4.4×10^{-3}	3.5×10^{-5}	3.7×10^{-3}	0.34

TABLE 2

CALCULATED pE BUFFERING CAPACITY (β_E) FOR VARIOUS REDOX COUPLES

AT THE LOWER BOUNDARY OF THE MIXING INTERVAL

Reaction	Reduced Species M (moles kg^{-1})	β_E (equiv. kg^{-1})
$\text{SO}_4^{=2-} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$	83×10^{-6}	12.2×10^{-3}
$\text{SO}_4^{=2-} + 10\text{H}^+ + 8\text{e}^- = \text{H}_2\text{S (g)} + 4\text{H}_2\text{O}$	17×10^{-6}	2.5×10^{-3}
$\text{N}_2 \text{ (g)} + 8\text{H}^+ + 6\text{e}^- = 2\text{NH}_4^+$	30×10^{-6}	0.8×10^{-3}
$\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- = \text{CH}_4 + 3\text{H}_2\text{O}$	3.6×10^{-6}	0.48×10^{-3}
$\text{CO}_2 \text{ (g)} + 4\text{H}^+ + 4\text{e}^- = \text{CH}_2\text{O} + \text{H}_2\text{O}$	30×10^{-6}	3.0×10^{-6}
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	8.2×10^{-6}	1×10^{-6}

$$- \sum_i \bar{n}_i \left(\frac{\partial \ln a_{xi}}{\partial \text{pE}} \right)_{\text{pH}} = 1.60 \times 10^{-2}$$

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FIGURE 1

Potential Temperature - Salinity Diagram

FIGURE 2

Profiles of Total CO₂, Ammonia and Phosphate for
Station 1466.

STATION 1466

FIGURE 3

Composite Profile of Total CO₂ Plotted Relative to Oxygen
Zero.

TOTAL CARBON DIOXIDE
(mM)

DEPTH RELATIVE TO OXYGEN ZERO

FIGURE 4

Composite Profile of Ammonia Plotted Relative to Oxygen
Zero.

FIGURE 5

**Composite Profile of Phosphate Plotted Relative to Oxygen
Zero.**

PHOSPHATE (μM)

FIGURE 6

Composite Profile of Chemosynthetic Rate as Determined by
Dark Uptake of ^{14}C - Bicarbonate, Plotted Relative to Oxygen
Zero.

MEASURED DARK CO_2 UPTAKE
($\text{g c} \times 10^{-3} \text{ m}^{-3} \text{ hr}^{-1}$)

DEPTH RELATIVE TO OXYGEN ZERO

FIGURE 7

Composite Profile of H_2S and O_2 Plotted Relative to Oxygen
Zero.

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THE DISTRIBUTION AND FLUX OF SOME TRACE ELEMENTS BETWEEN
DISSOLVED AND PARTICULATE PHASES IN THE BLACK SEA¹

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¹Manuscript received September 23, 1971.

Acknowledgements: This work was supported by the U.S. Atomic Energy Commission under Contract AT (30-1) - 4150 and by NSF grants GA-13574 and GA-1659.

Woods Hole Oceanographic Institution Contribution Number

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ABSTRACT

The trace element geochemistry of the Black Sea is dominated by the strong pycnocline separating the oxygenated and reducing environments. Using values of the vertical advective velocity and vertical coefficient of eddy diffusion derived from a model we have estimated the flux of dissolved sulfide, manganese, iron, copper and zinc through this interface. The calculated sulfide flux of $145 \text{ mMm}^{-2} \text{ yr}^{-1}$ is smaller than estimates of sulfide production, and of the same order of magnitude as sulfide loss by chemosynthesis, suggesting that this mechanism may be more important than mixing in removing sulfide from the system. From the manganese data we deduce that some 78% of the detrital load of rivers entering the Black Sea is deposited near the mouth of the river and only 22% is spread over the surface of the Black Sea. Given a mean sinking rate of 1000 m yr^{-1} the data on the distribution and elemental composition of particulate matter in the Black Sea is in agreement with estimates of river input.

INTRODUCTION

Our knowledge of the trace element geochemistry of the world's oceans is poor and the little data that are available show only small variations in the distributions of such elements as Cu, Zn, Fe, Mn, Ni and Co (Spencer and Brewer, 1969; Spencer, et al., 1970). The Black Sea, however, presents a special problem in that the area is small enough to be intensively surveyed, is subjected to large terrestrial run-off, and the deep waters are permanently anoxic. During cruise #69 of R/V ATLANTIS II to the Black Sea in March and April of 1969, we carried out a sampling program to study the trace element geochemistry of both the water masses and the suspended matter.

In a previous publication (Spencer and Brewer, 1971) we have discussed the distribution of dissolved Mn, Fe, Cu, Zn, Co and Ni in the Black Sea in terms of redox reactions taking place at the oxygen-sulfide boundary and a vertical advection diffusion model. Similarly, we have described the distribution of suspended matter in the Black Sea and determined the elemental abundances of Mn, Fe, Ca, Hg, Zn, La, Sb and Sc in this material (Spencer et al., 1971). Full details of the experimental methods and treatment of the data, together with a compilation of the raw data, are given in these papers.

In this contribution, we attempt to show the correlations that exist between the two sets of data and by means of the mixing model previously derived and mass balance calculations, examine the processes influencing the flux of elements through the sea to their sink in the sedimentary column.

COLLECTION OF SAMPLES AND ANALYSIS

Collection. - Sample collection has been described by Spencer and Brewer (1971). Briefly, 132 samples at 23 stations (see Ross and Degens, this volume, for station locations) were taken with 30 L P.V.C. Niskin bottles. Ten liters of each sample were run into clean linear polyethylene jerry cans and immediately filtered through a pair of pre-weighed 0.45 μ Millipore HA filters using nitrogen gas pressure, thus isolating the sample from oxidation and contamination. After filtration each sample was acidified to pH 1.8 with concentrated hydrochloric acid.

Analysis of Particulate Matter

The filters were dried at room temperature and weighed, the lower filter of the pair being used to provide a blank correction. Determinations of Mn, Fe, Co, Hg, Zn, Sc, La and Sb were made on 75 of these samples by means of instrumental neutron activation analysis using a Ge (Li) detector as described by Spencer, Brewer and Sachs (1971).

Analysis of Dissolved Trace Metals

Determinations of Fe, Cu, Zn, Ni and Co were carried out by the solvent extraction and atomic absorption procedure described by Brewer et al. (1969).

Analyses of dissolved manganese were made colorimetrically using a modified formaldoxime method (Brewer and Spencer, 1971).

HYDROGRAPHIC OBSERVATIONS AND VERTICAL MIXING MODEL

The hydrography of the Black Sea is dominated by the marked density gradient separating the saltier deep water from the fresher surface layers, thus inhibiting vertical mixing and permitting the deep water to become anoxic. The depth of this interface varies across the sea, being deeper close to the edge. Figure 1 illustrates this fact in presenting data for σ_θ , temperature and salinity for two stations; station 1436 close to the center and station 1469 close to the shelf. We have previously demonstrated that oxygen zero occurs at a constant density and temperature all over the Black Sea and hence, data from stations at widely different locations may be bulked on a single profile by assigning depths relative to oxygen zero as a common reference point. The assumption is made that the deep water is well mixed and that there are no horizontal gradients. Figure 2 shows potential density plotted in this way with data from 10 different stations.

The source of the salty bottom water is in the deep inflow of Mediterranean water through the Bosphorus and from the available data we have selected a best estimate for this inflow of about $190 \text{ km}^3/\text{year}$ (Bogdanova,

1961). This water sinks to a depth of 700-1000 meters and must be returned through the halocline to the surface layers by vertical advection and diffusion; if we assume an area of the upper boundary of the mixing interval of $3.7 \times 10^5 \text{ km}^2$ then we calculate an upward advective velocity of 0.5 m/year. In order to provide a more exact description we have fitted the vertical profiles of potential temperature and salinity with the vertical advection-diffusion parameter Z^* (Craig, 1969), the ratio of the vertical eddy coefficient (K) to the vertical advective velocity (W) (Spencer & Brewer 1971). The fit was made for six stations at different locations over the linear T-S region from about 80-350 m depth, and an average value for K/W of 0.09 km was found. With W at 0.5 m/year we calculate a vertical eddy diffusion coefficient in the main halocline as approximately $0.014 \text{ cm}^2/\text{sec}$.

Vertical Flux of Sulfide. - Having calculated K and W we can estimate the net upward flux (F) of a dissolved species (X) from its concentration gradient:

$$F(x) = K \frac{d(x)}{dz} + W(x) \quad \text{--- 1}$$

It is of particular interest to calculate the upward flux of sulfide. Figure 3 shows a plot of dissolved sulfide for several stations normalized

to oxygen zero, taking a concentration gradient of $.57 \text{ mM m}^{-4}$ and a lower boundary condition of 140 mM m^{-3} at 250 m below oxygen zero we calculate the upward flux of dissolved sulfide as $145 \text{ mM m}^{-2} \text{ yr}^{-1}$. This sulfide is lost by oxidation in the upper waters and in the steady state we have:

Sulfide production = sulfide loss by mixing + sulfide loss by chemosynthesis. Sorokin (1964) estimates total sulfide production in the sediments as 10^7 kg/day or $340 \text{ mMm}^{-2} \text{ yr}^{-1}$, a factor of 2-3 greater than our calculated loss at the upper interface. Deuser (1971) sets an upper limit on chemosynthetic fixation of organic carbon of $15 \text{ g Cm}^{-2} \text{ yr}^{-1}$. If we assume that 1 mole of sulfide is consumed in the chemosynthetic production of 1 mole of carbon this would indicate a sulfide consumption of approximately $530 \text{ mMm}^{-2} \text{ yr}^{-1}$. This assumption is made but the calculations show that chemosynthesis may well be more important than mixing in removing sulfide. The large scatter in our sulfide data precludes any more exact treatment of the mixing model for sulfide.

Suspended matter. - Figure 4 shows the dry weight of total suspended matter in the Black Sea. The highest concentrations are in surface waters near the shelf ranging from 1.0 to 0.1 mg/kg, deep water concentrations are about 0.1 mg/kg with a small but statistically significant increase with depth. This contradicts the observations of Shimkus and Trimonis (1972) who report values in excess of 3 mg/l in the deep water, but is in reasonable agreement with the data of Emelyanov (1962) for the surface waters. The maximum concentration recorded was to 0.96 mg/kg for station 1449 close to the mouth of the Bosphorus and at the pycnocline where the strong density gradient would be expected to hold up particulate matter.

From a study of core 1474 which represents sediment undisturbed by turbidity currents and slumps for the last 2000 years, Deuser (1971) has deduced a sediment accumulation rate of $100 \text{ g m}^{-2} \text{ yr}^{-1}$. Thus assuming a suspended matter concentration of $1 \times 10^{-4} \text{ g/kg}$ and a water depth of 2000 m we calculate an average particle sinking time of approximately 2 years. The particulates consist of clastic and argillaceous material from river input, carbonaceous material and organic detritus from the surface layers and a manganese oxide phase formed at the helocline by in situ precipitation from Mn (II) transported from the reducing environment below.

Dissolved iron and manganese.—Figure 5 shows the vertical distribution of dissolved iron and manganese and Figure 6 shows data on particulate iron and manganese. The marked peak in particulate manganese at about 50 m above oxygen zero is due to precipitation of MnO_2 from the upward transport of dissolved Mn (II) from the anoxic water below. Once formed the particles of MnO_2 sink and redissolve in the reducing environment; the chemical kinetics and physical transport rates of this system result in the unique shape of the dissolved manganese profile shown in Figure 4.

We have fitted the profile of dissolved manganese with the solution of a modification of the equation for a stable conservative tracer

$$K \frac{\partial^2 c}{\partial z^2} - w \frac{\partial c}{\partial z} + J_0 e^{-\mu z} = \frac{\partial c}{\partial t} = 0 \quad \text{---}^2$$

(Craig and Weiss, 1970) allowing for an exponentially decreasing in situ production rate (J) of dissolved manganese from dissolution of the

particulate flux. The two parameter fit, solving for J_0/W and μ gave values of $0.9 \mu \text{ kg}^{-1}$ and -38 km^{-1} respectively, thus permitting calculation of

$$J = 4.5 \times 10^{-4} e^{.038z} \quad \text{_____}^3$$

where z is the distance in meters from the lower boundary of the mixing interval, and giving a median in situ production rate of $17 \mu \text{g kg}^{-1} \text{ yr}^{-1}$ at a depth close to 2 m above oxygen zero.

The profile in dissolved iron is similar in shape, possessing a sharp break just at oxygen zero and increasing to a maximum about 120 m below it, however, our data show greater scatter and we have not been able to characterize the profile as precisely as for manganese. Attempts to fit the equation used for manganese were not successful; a much smaller exponential is required to reproduce the linear portion of the profile from oxygen zero to 120 m below it, coupled with a much larger term for J_0/w (indicating a greater flux of iron). However, this system does not show the sharp break under the dissolved peak which reduces the iron concentration to approximately $10 \mu \text{g/kg}$ at 500 m below oxygen zero. Some other process must be taking place and it seems likely that reduction of Fe(III) to Fe(II) and solution of the ferrous iron takes place rapidly on entering the sulfide zone until saturation with respect to an insoluble phase (probably FeS) occurs and precipitation begins, reducing the Fe (II) concentration sharply.

The net upward flux of manganese and iron can be calculated from our values for K and W and the concentration gradient and concentration from the data shown in Figure 5. We calculate an upward flux of manganese of $675 \text{ mg m}^{-2} \text{ yr}^{-1}$ and for iron $43.3 \text{ mg m}^{-2} \text{ yr}^{-1}$. The upward flux

of dissolved manganese oxidizes and maintains a "standing crop" of about 60 mg m^{-3} of manganese dioxide, thus in order to maintain this steady state we arrive at a sinking rate of approximately 11 m yr^{-1} for this fine grained precipitate. If we assume the same oxidation kinetic for iron as for manganese then we would anticipate a standing crop of precipitated ferric hydroxide of approximately 4 mg m^{-3} in the water column just above oxygen zero. The values we observe range from 4 to 70 mg m^{-3} and there is no evidence of a peak similar to the one observed for manganese, the precipitate being masked by the iron associated with the silicate detrital flux from above.

Copper and zinc.—The distributions of dissolved copper and zinc are shown in Figure 6 and demonstrate the obvious effects of precipitation at the oxygen sulfide boundary. We have attempted to calculate the equilibrium concentrations for the various metal-sulfide species and the data are given in Table 1. It is obvious that larger amounts are present naturally than we would expect from these simple calculations due to the formation of soluble thio-metallic complexes, although dissolved iron appears too saturated with respect to FeS.

Using the simple flux equation (1) it is possible to calculate the flux of copper and zinc down through the halocline (see Table 2).

Taking the values for Cu and Zn from the data shown in Figure 6 we calculate a flux of $0.6 \text{ mg m}^{-2} \text{ yr}^{-1}$ for Cu and $1.0 \text{ mg m}^{-2} \text{ yr}^{-1}$ for Zn.

Cobalt and nickel.—Data for dissolved Co and Ni are shown in Figure 7. The data for Co seem to be about one order of magnitude higher than reported values for the world ocean (Spencer et al., 1970).

The data show a maximum just below oxygen zero and there is no obvious evidence of precipitation due to sulfide. We have tentatively ascribed the peak in Co as arising from adsorption of Co on to the manganese oxide solid phase just above oxygen zero, transport of the metal through the halocline by sinking solid particles and release of Co on solution of the manganese. The profile of nickel is similar to that in the world ocean varying smoothly from surface values of approximately $1.6 \mu\text{g/kg}$ to about twice that value at depth.

River input of particulate matter.—Having fitted the dissolved manganese profile with equation 2 and obtaining the value for J given in 3 we are able to calculate the flux of particulate manganese required to dissolve and maintain the profile in the assumed steady state.

This is given by the integration of 3 over the entire water column

$$F_{\text{Mn}_p} = \int_{-2000}^{295} 4.5 \times 10^{-4} e^{0.38z} dz = 875 \text{ mg m}^{-2} \text{ yr}^{-1}$$

The difference between this value and the amount of manganese generated by precipitation in the water column must equal the detrital flux from above, which amounts to $200 \text{ mg m}^{-2} \text{ yr}^{-1}$.

Data on the river discharge of trace elements both in the dissolved and particulate form has been given by Konovalov and Ivanova (1970). They estimate a total river input of particulate manganese into the Black and Azov seas as $366 \times 10^3 \text{ tons yr}^{-1}$, or $886 \text{ mg m}^{-2} \text{ yr}^{-1}$. Thus in order to fit our model we suggest that only 22% of this river input

stays in suspension and spreads over the basin and some 78% of the detrital load is deposited on the shelf areas and close to the river mouth.

Using this same fraction we calculate the quantities of Co, Cu and Zn transported and the data are given in Table 3.

The results are consistent with other observations. The detrital flux of copper is about equal to that from sulfide precipitation, while the detrital flux of zinc is approximately 10 times greater. Hirst (1972) has carried out a series of analyses of Black Sea sediments and described a factor analysis of the data showing that Cu is closely associated with a sulfide factor whereas zinc is not. We have no evidence of cobalt precipitation in the water column and thus the cobalt present should result entirely from river input. Assuming a sinking rate of 1000 m yr^{-1} we calculate a standing crop of cobalt of 10 ng kg^{-1} , in fair agreement with observed data.

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TABLE 1

Comparison of Observed and Calculated Equilibrium Concentrations

Species	Solubility Product Ksp	Calculated value (M) (pH=8, $\Sigma s=10^{-4}$ M)	Observed value (M)
ZnS	$10^{-23.8}$	$10^{-14.7}$	10^{-8}
CuS	$10^{-35.4}$	$10^{-25.3}$	$10^{-8.3}$
CoS	$10^{-20.4}$	$10^{-10.3}$	10^{-8}
NiS	$10^{-18.5}$	$10^{-8.2}$	$10^{-7.3}$
MnS	$10^{-12.6}$	$10^{-2.5}$	$10^{-5.4}$ to $10^{-5.1}$
FeS	$10^{-17.0}$	$10^{-6.9}$	$10^{-6.8}$ to $10^{-6.1}$

TABLE 2

Vertical Transport of Elements through Halocline
($w=0.5$ m/yr $K=0.14$ cm²/sec 2 positive upward)

Species (x)	$\frac{dx}{dz}$ mg m ⁻⁴	Boundary value mg m ⁻³	Flux mg m ⁻² yr ⁻¹
H ₂ S	.57 (mM)	140 (mM)	145 (mM)
Mn	10	450	675
Fe	.473	45	43.3
Cu	.02	3	-0.6
Zn	.01	3	-1.0

TABLE 3

River Input of Particulate Trace Elements Into the Black Sea

Element	Input ($\text{mg} = \text{yr}^{-1}$)	
	Total	Calculated flux through halocline
Mn	886	200.0
Co	46	10.4
Cu	2	4.6
Zn	506	114.0

FIGURE CAPTIONS

Figure 1. Profiles of S_{O_2} , $T^{\circ}\text{C}$, and DO for two Black Sea stations.

Figure 2. Profile of DO from 10 stations normalized to oxygen zero.

Figure 3. Profiles of dissolved sulfide normalized to oxygen zero.

Figure 4. Dry weight of suspended matter.

Figure 5. Profiles of dissolved (a) manganese and (b) iron.

Figure 6. Profiles of particulate (a) manganese and (b) iron.

Figure 7. Profiles of dissolved (a) copper and (b) zinc.

Figure 8. Profiles of dissolved (a) cobalt and (b) nickel.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5A

Figure 5B

Figure 6A

Figure 6B

Figure 7A

Figure 7B

Figure 8A

Figure 8B