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SOLUBLE IRON IN COASTAL WATERS¹

BY

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ABSTRACT

Soluble iron, defined as the amount of the element found in a unit volume of millipore-filtered sea water, after oxidation of organic matter, has been determined on samples collected in inshore waters of the State of Washington. After filtration the samples were oxidized. The particulate matter and its iron content were also determined. Bathophenanthroline was the reagent used.

Analyses showed a variation in soluble iron ranging from 5.5 to 32 $\mu\text{g/l}$; the particulate matter varied from 700 to 2,000 $\mu\text{g/l}$ and contained from 2.8 to 13.3% of iron. While the general conclusions on the distribution of iron in the waters of the State of Washington may be valid, such values for soluble iron are high in the light of recent studies by Lewis and Goldberg.

INTRODUCTION

In earlier studies on the occurrence of iron in sea water (Thompson and Bremner, 1935a, 1935b), Whatman No. 42 filter paper was used to remove suspended matter, and the iron, determined in the filtrate after oxidation of organic matter, was considered as soluble iron. However, Armstrong and Atkins (1950) stated that such filters will permit the passage of about 4% of the suspended matter. Subsequently Goldberg *et al.* (1952) and Fox *et al.* (1953) demonstrated that HA millipore filters were preferable for removing suspended matter. Accordingly, Lewis and Goldberg (1954) defined soluble iron as the amount found in a unit volume of sea water which had been passed through a millipore filter. Unpublished data by T. Laevastu and C. A. Barnes indicate considerable variation in the amounts of particulate matter retained by fine filter papers such as Whatman No. 42; these investigators often obtained values higher than the 4% suspended matter noted by Armstrong and Atkins as passing through the filter. Observations by Laevastu and Barnes on the use of millipore filters were in agreement with those of Goldberg *et al.* and Fox

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et al. Thus, the definition of soluble iron as given by Lewis and Goldberg is preferred to that given earlier by Thompson and Bremner.

Lewis and Goldberg showed that particulate iron varied considerably in waters of the North Pacific; they also implied that soluble iron is rather uniformly dispersed in oceanic and coastal waters. Thompson and Bremner showed a decided seasonal variation in soluble iron, the range being from 14.5 μg during the spring and summer months to 41.8 μg for the fall and winter months. Thus, these data show a marked variance from those of Lewis and Goldberg. Furthermore, Lewis and Goldberg found that soluble iron in California coastal waters was 3.4 μg while Thompson and Bremner reported 6.1 μg soluble iron for waters some 100 miles off the coast of the State of Washington. Considering the differences noted, re-examination of the occurrence of soluble iron in the sea waters of Washington seemed desirable. The same method as that employed by Lewis and Goldberg was used.

METHOD OF ANALYSIS

Determination of Soluble Iron and Particulate Iron. The method of Lewis and Goldberg was applied in the present study with the exception of the following minor changes: (1) Because of the relatively large blank corrections due to the iron content of the perchloric acid, sea water samples of 200 ml or more were used; these had been filtered through HA millipore filters. (2) Both particulate iron and soluble iron were determined by the bathophenanthroline method.

Determination of Particulate Matter. Millipore filters, HA type, were dried at 20°C in a vacuum desiccator containing a solution of sulfuric acid which had a water vapor pressure equivalent to 60% of the relative humidity. Each filter was weighed to constant weight after it had been dried and 1.5 liters of freshly collected sea water were passed through it. The filter and the particulate matter retained by it were washed with distilled water to remove all soluble salts, after which the filter was again dried in a vacuum desiccator to constant weight. The difference in weight gave the total particulate matter which was further checked by an optical method to be described in a future paper by one of us (TL).

The particulate matter and the millipore filter, after weighing, were digested with perchloric acid as described by Lewis and Goldberg; the resulting solution was then diluted to 100 ml with iron-free distilled water, and 10 ml aliquots were taken for analysis with the bathophenanthroline reagent.

Collection of Samples. Surface samples were collected with a plastic bucket and subsurface samples with a nonmetallic water sampler described by Thompson and Chow (1955); thus, the possibility of contamination from extraneous particles containing iron or iron rust was eliminated. The plastic bucket and the sampler were washed occasionally with dilute hydrochloric acid and rinsed with distilled water. Samples were prepared for analysis immediately after collection. All samples ranged from 16.0 to 16.8 Cl‰, except the surface sample at Brown Point which had a chlorinity of 14.0‰.

Errors that may occur in iron analyses if samples are stored in glass bottles have been described by Goldberg (1952). Armstrong (1957) calls attention to the deposition of ferruginous matter on polyethylene exposed repeatedly to sea water, and this observation has been confirmed by us.

DISCUSSION OF RESULTS

Results of analyses are shown in Table I. The soluble iron content varied from 5.5 to 32 $\mu\text{g}/\text{l}$ with an average of 17.8 μg for all stations. These values are about 40% less than those reported by Thompson and Bremner, who used Whatman No. 42 filter paper; on the other hand, these are much greater than the 3.4 μg iron values given by Lewis and Goldberg. Armstrong reports values of 4 to 8 μg soluble iron per liter.

Suspended or particulate matter in the samples ranged from 700 to 2,000 $\mu\text{g}/\text{l}$, the mean being 1,440 μg . The iron content of this material varied from 51 to 163 $\mu\text{g}/\text{l}$, with a mean of 114 μg , or, from 2.8 to 13.3%, with a mean of 6.8%. Armstrong and Atkins also found considerable fluctuations in the iron content of suspended material. However, their values were obtained after the particulates had been ignited. Such ignition caused the destruction of organic matter and produced other chemical changes. Their mean value was 10.5%; this is higher, as would be expected due to ignition, than our value for air-dried material.

Samples of millipore-filtered sea water were analyzed for soluble iron both with and without oxidation with perchloric acid. The data, shown in Table II, demonstrate that only 25% of the total soluble iron is determinable on the nonoxidized samples. The undeterminable iron in such waters exists largely in the form of ferruginous organic complexes which will not react with reagents used for the estimation of iron. Such reactions will readily occur upon the destruction of the complexes by oxidation.

Simons *et al.* (1953) determined soluble iron in offshore waters in the western Atlantic by using Whatman No. 42 filters to remove

TABLE I. ANALYSES OF SEA WATER SAMPLES FOR PARTICULATE MATTER,
PARTICULATE IRON, AND SOLUBLE IRON
15 March 1955

<i>Location, including Latitude and Longitude</i>	<i>Depth (m)</i>	<i>Particulates dry ($\mu\text{g/L}$)</i>	<i>Particulate iron ($\mu\text{g/L}$)</i>	<i>Iron in dry particulates (%)</i>	<i>Soluble iron ($\mu\text{g/L}$)</i>
Strait of Juan de Fuca					
Green Point	0	1,500	93	6.2	5.5
48°10' N, 123°19' W	100	1,850	111	6.0	27.0
Admiralty Inlet					
Port Townsend					
48°8' N, 122°45' W	0	—	—	—	9.0
Point No Point					
47°54' N, 122°30' W	100	1,100	53	4.8	29.0
Hood Canal					
Brown Point	0	2,000	125	6.2	24.0
47°45' N, 122°45' W	100	1,800	51	2.8	32.0
Tabook Point					
47°45' N, 122°50' W	100	1,100	108	9.8	9.0
Tekiu Point	100	700	93	13.3	15.0
47°35' N, 122°59' W	0	—	—	—	15.5
Tahuya River					
47°22' N, 122°56' W	0	1,600	163	10.2	13.0
Lynch Cove					
47°25' N, 122°56' W	0	—	—	—	7.5
Puget Sound					
Alki Point	0	1,000	60	6.0	11.0
47°35' N, 122°26' W	100	1,600	88	5.5	32.0
Gordon Point					
47°10' N, 122°39' W	0	1,550	59	3.8	20.0
Mean		1,440	114.1	6.78	17.8

TABLE II. SOLUBLE IRON, DETERMINED (A) WITHOUT OXIDATION AND (B) AFTER
OXIDATION WITH PERCHLORIC ACID
15 March 1955

<i>Place of collection</i>	<i>Depth (m)</i>	<i>A (Fe. $\mu\text{g/L}$)</i>	<i>B (Fe. $\mu\text{g/L}$)</i>
Brown Point	0	5.7	24
Alki Point	0	5.7	11
Alki Point	100	4.0	32
Lynch Cove	0	2.8	7.5
Tekiu Point	0	2.5	15.5
Port Townsend	0	2.0	9.0
Mean		3.8	16.5

suspended matter and by using o-phenanthroline as the reagent for estimating iron. They made no attempt to destroy the organic matter by oxidation. Their values for soluble iron are thus very low and are in agreement with those shown in Table II for analyses made when the samples were not treated with perchloric acid.

Cooper (1948) has discussed the various forms in which iron may occur in sea water, and recently Armstrong has studied methods for treatment of sea water samples so that the total soluble iron can be determined.

Iron analyses, compiled by Lewis and Goldberg from different oceanic areas by previous investigators, show a wide range of variability. The anomalies may be attributed partially to different methods of analyses and possibly to improper treatment and storage of samples; nevertheless, the results of individual investigators indicate that a wide range of iron concentrations may actually exist.

Fleming (1948) has described the differences that may exist between coastal and offshore waters. He stressed the great range and variability of conditions for inshore waters and thus suggested the possibility of considerable regional as well as seasonal variation. It is believed that such variations may be reflected in the large differences in the quantities of particulate as well as soluble iron. This is substantiated by Vinogradov (1944), who states that the concentration of iron as well as that of other trace elements may show large ranges not only as to area but also as to depth.

Data presented herein and data previously reported for waters off the coasts of the State of Washington, British Columbia, and southeastern Alaska (Thompson and Bremner, 1935b) show considerable fluctuations of particulate and soluble iron. Both forms of iron tend to increase with depth, and organic matter plays an important role in regulating the concentration of soluble iron.

The greater concentration of soluble iron in coastal and inshore waters may be attributed to the higher production of organic matter in these areas; to the halmirolysis of particulate matter; to the biological assimilation of the iron in particulates, which, on later decay of organisms, returns iron in soluble form to sea water; and to drainage from adjacent land areas.

The removal of iron from sea water may be attributed to precipitation as hydrated ferric hydroxide or as hydrosols after decomposition of organic complexes; to scavenging by calcium carbonate, clay minerals and biogen suspended matter; and to biological assimilation. Volcanic submarine activity may cause local differences, especially in deep water, as shown by Buljan (1954).

Knowing the amount of particulate iron present in oceanic waters

TABLE III. DISTRIBUTION OF SOLUBLE IRON IN WATERS AT DIFFERENT DEPTHS IN SOUTHERN PUGET SOUND
28 May 1955

<i>Location</i>	<i>Depth (m)</i>	<i>Soluble iron ($\mu\text{g/L}$)</i>
Whitman's Cove		
Lat. 47°13' N	0	4.7
Long. 122°48.8' W	5	3.5
	10	6.7
	20	9.0
	30	8.5
	40	7.0
Devil's Head		
Lat. 47°10.0' N	0	6.7
Long. 122°47.3' W	5	5.7
	10	12.0
	25	6.3
	50	6.7
	75	8.0

and the percentage of iron in suspended matter, it may be possible to estimate the amount of suspended matter and to aid in the solution of the problem brought into being by the controversies of Kullenberg (1953) and Arrhenius (1954) concerning the deposition of deep sea sediments. While the amount of data may be considered meager and from widely different sources, a computation indicates an interesting situation. By using the Lewis and Goldberg values for the amount of particulate iron ($4.5 \mu\text{g/l}$) as representative for Pacific oceanic waters as well as the mean value of 6.8% for the iron in suspended matter (see Table I), computation gives $66 \mu\text{g/l}$ of suspended matter for offshore waters. This value is relatively close to that of $56 \mu\text{g/l}$ which Kullenberg obtained by direct measurement.

For the treatment of sea water samples for iron analysis, it is the opinion of the present authors that the use of sulfuric acid, as outlined by Thompson and Bremner (1935a), is to be preferred to that of perchloric acid. The former reagent can be prepared or secured practically free of iron; the latter reagent has certain advantages, but the high blank determinations for iron makes its use less desirable. As indicated by Armstrong, phenanthroline is the preferred reagent for the estimation of iron.

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