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EVIDENCE FOR CHEMICAL FRACTIONATION AND NONCONSERVATIVE DISTRIBUTION OF FE, MN, CU, AND ZN IN COASTAL SEAS

by

© John T. Hoff

Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Oceanography at Dalhousie University, March, 1977.

Approved by:

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Abstract

Three investigations relating to the behavior of Fe, Mn, Cu, and Zn in coastal waters are presented: a spatial distribution study of surface waters in the Gulf of St. Lawrence, a temporal study of the spring flowering in St. Margaret's Bay, Nova Scotia, and a laboratory study of aerosol fractionation of dissolved transition metals. It was concluded that: Fe and Mn are clearly nonconservative in both environments, the time scale of removal being less than one year. Chemical fractionation of dissolved Cu in coastal seawater does occur, but its magnitude is probably not sufficient to account for observed enrichments of Cu in the marine atmosphere. The chemical mechanism of fractionation involves metal-binding organic colloids which sequester a significant fraction of dissolved Cu in coastal seawater.

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Introduction

Transition metals are introduced into the oceans principally via rivers and the atmosphere. The ultimate fate of dissolved trace metals in the ocean is incorporation into the sediments. The residence times of some transition metals are on the order of or less than the mixing time of the oceans, which means that spatial and temporal inhomogeneities may be expected. The oceanographic distribution of a nonconservative element is influenced by the mode of introduction, the mechanism of removal, and any involvement in internal cycling processes.

The observation that transition metals are enriched in the sea surface microlayer (e.g. sea slicks) provided the main impetus for this research. Microlayer enrichments imply sea-to-air fractionation, and chemical fractionation might be the reason for the observed enrichments of certain metals in the marine atmosphere. Sea surface microlayer and aerosol enrichments may be an indication of metal-organic complexes in seawater. These could be the product of biological fixation analogous to organic nitrogen and phosphorus. Biological utilization of transition metals might cause their oceanic distributions to resemble those of nitrogen, phosphorus, or silicon. These are the underlying ideas that stimulated the three investigations composing this thesis.

I. Chemical Fractionation of Dissolved Transition Metals

The Natural Occurrence of Chemical Fractionation

To test whether aerosol fractionation occurs naturally in coastal marine waters, a series of experiments were performed in conjunction with the regular sampling program in St. Margaret's Bay in the Spring of 1976. Large samples of seawater were taken with the aid of the "Top Drop Niskin" sampler, usually from 5 metres depth, brought back to the laboratory in acid-washed 20 litre polyethylene carboys, and subjected to experiments the same day. The apparatus consisted of a 1 1/3 metre Plexiglas column which was fitted with a polyethylene frit at the bottom and a polyethylene collector at the top. Filtered pre-humidified air or nitrogen was introduced into a full column of seawater. Bubbles emanating from the frit rose to the surface where they produced a spectacular fountain of jet droplets. The jet droplets impacted onto the undersurface of a collecting roof made of polyethylene film which ducted the sample into a polyethylene vial. An 8 ml sample of aerosol was generated from 9.5 litres of seawater; trace metals were determined on aliquots of each by methods described in the Appendix. The fractionation factor, F, is calculated by taking the simple ratio of the two concentrations.

Two variations on this theme were employed, depending on whether the seawater used in the column was pre-filtered. Using unfiltered seawater, the aerosol produced was enriched in both dissolved and particulate constituents, so it was analyzed for dissolved and particulate trace metals. Fil-

[illegible]ration of the small aerosol sample was accomplished with a disposable plastic syringe and Swinnex filter holder. Nitrogen gas was used throughout these experiments. On October 9, 1975 a thirty-litre carboy was filled with surface water collected from a rowboat about 15 metres offshore in Sandy Cove. Three trials were made utilizing unfiltered Sandy Cove water, and trial one is identical experimentally with unfiltered water experiments in St. Margaret's Bay. Trials two and three differ in that the aerosol samples were not filtered but analyzed "as is" for dissolved trace metals. Air was the bubbling gas used in these trials.

Analysis of aerosol samples for dissolved trace metals was accomplished by spiking four 47 ml aliquots of original filtered seawater with one ml aliquots of the aerosol sample, which gave a linear relationship similar to the method of standard additions. Error statistics were computed for the fractionation factor, F, by methods described in the appendix. The analysis of Sandy Cove samples consisted of comparing aliquots of aerosol and original seawater directly; uncertainties in measuring F by this procedure are assumed to be ± 10%. All of the data from bubbling experiments performed on St. Margaret's Bay water and Sandy Cove water are compiled in Table 1.

These data form a basis for discussing whether aerosol droplets produced by bubbles bursting at sea are enriched in transition elements relative to sea salt. Consider first the fractionation of dissolved trace metals. Variability is a key factor in the interpretation of environmental data

Table 1 Fractionation Factors for Dissolved and Particulate Trace Metals Using Seawater Samples from St. Margaret's Bay and Sandy Cove, Nova Scotia. The values in parentheses refer to the fractionation of particulate metals.

Date	Depth	Filtered/ Unfiltered	Fe	Mn	Zn	Cu	Al
				St. Margaret's Bay			
9Mar76	5 m	f.	2.8±1.	<2.1	<1.9	17.±3.	
16Mar76	5 m	f.	3.3±0.5	<2.	9.±1.5	9.±1.	
16Mar76	5 m	unf.	2.8±0.4 (192.)	<1.9 (310.)	5.8±1. (249.)	26.±2.	(226.)
23Mar76	5 m	f.	<1.4	<1.7	<2.5	18.±1.	
23Mar76	5 m	unf.	<1.6 (248.)	1.2±0.6 (329.)	<1.8 (101.)	20.±1.	(231.)
2Apr76	5 m	f.	<1.9	<2.2	4.4±1.	45.±3.	
2Apr76	5 m	unf.	4.3±0.5	24.±2.	25.±3.	30.±1.	
5Apr76	5 m	f.	10.±1. (45.4)	<2. (69.2)	1.2±0.5 (35.3)	35.±3.	
15Apr76	5 m	unf.	<1.6 (214.)	17.±3. (363.)	3.±0.5 (113.)	32.±3.	(198.)
15Apr76	5 m	unf.	<1.5 (198.)	21.±5. (369.)	5.2±0.3 (120.)	44.±6.	(174.)
15Apr76	25 m	unf.	1.3±0.1 (122.)	82.±13. (194.)	2.5±0.5 (86.)	39.±1.	(123.)
26Apr76	5 m	f.	1.7±1.6	5.8±1.	2.4±0.7	19.±1.	
				Sandy Cove			
9Oct75	surface	unf. (1)	9.4±0.9	5.5±0.6	4.1±0.4	68.±7.	(290.)
9Oct75	surface	unf. (2)	115.±11.	15.3±1.5	14.±1.4	50.±5.	
9Oct75	surface	unf. (3)	155.±16.	14.7±1.5	14.±1.4	52.±5.	

such as these. The analytical uncertainty (standard deviation of the analysis) provides a criterion for evaluating whether the measured enrichment factor is significantly different from unity. Such is the case when $F - s_1 > 1$. By this test, Cu showed significant fractionation every time, Zn in about 3/4 of the experiments, and Fe and Mn only half of the time. The enrichment of Cu is the most marked in magnitude also, ranging from 9 to 68 with a mean of 30. With respect to magnitude, Mn, with a mean of 17 is the second best fractionator. Zn and Fe are similar, with means of 4.4 and 3.3 respectively. Replicate runs on the column were not made, so the overall experimental variability cannot be evaluated, but there generally seemed to be reasonable agreement in comparing similar trials. It is therefore difficult to guess the amount of true environmental variability, but judging from the range of values which occurred for any given element it is almost certain to be appreciable. The figures for Cu indicate an overall variability of more than 500%; this is thought to be far in excess of that which can be accounted for by the experimental variables. Of some interest are the particularly high F values for Mn on April 15 and the seemingly higher values for both Mn and Cu during the latter half of the sampling period, when the water was biologically active (see "Trace metal observations in St. Margaret's Bay"). Although little can be concluded about the correspondence of the phenomenon with environmental factors with which it could be linked, it is certain that fractionation of dissolved transition metals occurred for some of the metals some of the time. Dissolved Cu performed consistently and dramatically, leading me to choose it for further studies and also to speculate about the oceanographic significance of the sea-to-air fractionation of dissolved Cu.

Considering next the fractionation of particulate trace metals, it is obvious that F(particulate) is greater than F(dissolved) where both data are available for comparison. The difference seems to be extreme, as much as two orders of magnitude, and this raises the question of whether F(particulate) will always be greater than F(dissolved). Since the factors responsible for controlling the magnitude of F(particulate) have not been investigated, it is not possible to speculate at this time. The removal of particulate matter from the column of seawater was very efficient, being in the neighborhood of 8-25% in the half hour of bubbling that yielded 8 ml of aerosol. In terms of total metal transported from the bulk to the dispersed phase, the fractionation of PTM was sometimes more significant than that of DTM. The concentration of particulate Fe greatly outweighed that of dissolved iron in the aerosol samples. This was also true to a lesser extent for Mn, but Zn was about equally apportioned between the two forms. If it can be assumed that $Al_d \gtrsim Fe_d$, and if $Cu_p \lesssim Zn_p$ (Wallace et al, 1976), then Al would be expected to resemble iron in this respect, and Cu would be like Zn. The apportionment of metal in the aerosol thus followed the rule that the particulate form was relatively more enhanced. Typical of coastal waters, the particulate load of these waters was quite high (~ 1 ppm), and the aluminosilicate fraction was substantial (~ 10%). The above conclusions may not apply to the open ocean, where the particulate load is much less and more of it is organic.

There appears to be some evidence, in the small amount of data present on F(particulate), that the four metals tend to fractionate with different F factors. This can be demonstrated at the 95% confidence level by an analysis of variance. There is no significant difference between Fe and Al, indicating a common carrier, but Mn differs from Zn at the 98% level. The relative order of F(particulate) for the metals is Mn > Al ~ Fe > Zn. The nature of the process which discriminates between these metals is not known. It could be a discrimination based on size or type of particle, or it might involve some kind of interaction between DTM and PTM. In this connection, it is interesting to recall the foam fractionation experiments of Wallace and Duce (1975). Using Narragansett Bay seawater, they found that the foam fraction had higher PTM/C ratios than the original seawater and suggested that the flotation process selectively removed particles with a greater trace metal/carbon ratio. Note that Sandy Cove water trials 2 and 3 indicate higher fractionation of Fe, Mn, and Zn than trial 1. This is attributed to the solvent extraction of small amounts of metal from the particulate matter present in the latter two aerosol samples. There is a distinct possibility that some DTM is converted to PTM in aerosol samples. This might cause the enrichments for filtered seawater experiments to be greater than those for unfiltered experiments, but this was not observed. The resolution of this point requires further experimentation.

In comparing the fractionation of dissolved and particulate forms, it is concluded that for some metals, i.e. Fe and Al, the bubble transport of particulate matter is quantitatively more important, while for other metals, i.e. Cu and Zn, the contribution of dissolved species may be at least as important. It should be mentioned that the situation may differ in the open ocean, and that the chemical forms of trace elements in the marine atmosphere are as important as their concentrations since this governs their fate on reintroduction.

The Physical Chemical Explanation of Aerosol Fractionation

Given the existence of aerosol fractionation of dissolved transition metals in seawater, the next logical question to ask is, how does it occur? A thorough explanation of this phenomenon of course presupposes knowledge of the chemical species involved, but a definitive knowledge of the chemical forms of transition elements in seawater has not yet been attained (Stumm and Brauner, 1975). The experimental approach which was accordingly adopted was to study the system as a "black box". By manipulating those variables which are accessible and causative, then observing how the system responds, one can gain clues about the nature of the mechanism. The bubble fractionation system lends itself to this approach, because the main variables can be kept under control to yield reproducible results.

One usually begins such an investigation with a preconception based on general observations and a theoretical knowledge of the nature of the chemical system. In retrospect, it has been observed that the aerosol is also enriched in dissolved organic matter, which wets the polyethylene surface of the collector, is sometimes yellow and fishy smelling, sometimes clear, sometimes opalescent, etc. Trace metal enrichment in the aerosol has been found to decrease as successive samples of it are taken, most rapidly at first, and gradually reaching zero after exhaustive bubbling. Also diminishing as bubbling continues is the rate of aerosol formation. For typical experimental conditions, the average bubble diameter is about one milimetre. Both jet and film drops are possible, although it is believed that the aerosol samples collected consist almost entirely of jet drops. There two reasons: jet drops are ejected to sufficient heights (2-5 cm) to impinge onto the collector, and jet drop formation is the predominant process under normal conditions. At the beginning of a bubbling run, jet drop ejection is particularly vigorous; as bubbling continues, however, the jet droplets become larger and less numerous. This trend continues until a froth forms at the interface; then film drops predominate. High enrichments of both metals and organic matter may be linked. Of particular advantage is the fact that there are similarities between the system under investigation and others which have been studied before for their technical interest (Lemlich, 1972). The general principles of foam and froth flotation are applicable to the problem.

Since bubble fractionation of particulate matter has been seen to be so effective, is it possible that the dissolved fractionation already seen is residual particulate fractionation due to the inefficiency of filtration in removing all particles? This is unlikely for two reasons: As noted previously, filtration of the aerosol does not remove the enrichment. Contamination of the dissolved fraction by the particulate fraction is also very unlikely for metals such as Cu and Zn, whose particulate concentrations are typically much less than the dissolved (see Table 10, Appendix). Therefore, dissolved fractionation is caused by species which are less than .45 µm; this includes colloidal matter and truly dissolved ionic species. If flotation is truly ionic, this implies the existence of a collector (surface active molecule of opposite charge) and a colligend (metal ion). If flotation is colloidal, it could be either an inorganic colloid, e.g. $Fe(OH)_3$, or an organic one, e.g. a large protein molecule. Thus surface activity and trace metal association are both prerequisites for fractionation.

In the following series of experiments, the main variables which were placed under experimental control were: pH, the addition of artificial surfactants, ultrafiltration, and photo-oxidation with u-v light. By convenience and necessity, all of the experiments were performed on .45 µm filtered tap seawater. Tap seawater is pumped from an inlet deep in the Northwest Arm via PVC pipes through a sand filter. Although tap seawater drawn from the Oceanography building's lines would not be expected to duplicate natural seawater for many reasons, it did in fact produce enrichments of Cu very similar to those found using St. Margaret's Bay water and Sandy Cove water. Since the concentrations of Fe, Mn, Cu, and Zn in filtered tap seawater were approximately the same as typical coastal seawater, there is no evidence of contamination from the system which delivers seawater to the laboratory. The analytical observations were limited to Fe and Cu, since at the start of these experiments in September 1976 both of these metals produced high enrichments whereas Mn and Zn did not.

Three experiments were carried out in the attempt to determine whether pH has any control over the magnitude of the F factor. For the experiment beginning on September 10, five carboys of filtered tap seawater provided ten bubbling runs with the column. A constant volume of aerosol, 8 ml, was collected each time to aid reproducibility. The pH was adjusted with Aristar HCl to enable replicate runs to be made at pH = 8.6, 7.7, 4.0, 2.3, and 2.0. Nitrogen gas was used as the bubbling agent. The purging of CO_2 accounts for the unusually high pH of the unacidified seawater. For the experiment beginning on September 20, five carboys of filtered tap seawater were used to make replicate runs at pH = 8.2, 7.4, 7.1, 2.6, and 1.9. Air was used this time instead of nitrogen. The other difference between September 10 and 20 is the way in which five pH values were distributed among five carboys. On September 10, two of the carboys were split--half at pH 8.6 and the other half at pH 2.0. On September 20, only one of the five carboys was not split into high and low pH runs. The addition of a large amount of concentrated HCl necessary to bring the pH down to 2.0, contributed substantial amounts of Fe and Cu to the sample. This was compensated for in the calculation of F. The F factor was measured by comparing an aliquot of unspiked seawater from the column with another which contained a 1 ml spike of the aerosol sample. The extractions (see Appendix) were done in duplicate at constant volume and constant pH in 30 ml Quickfit tubes. The pH was measured after each run using water which was in equilibrium with the bubbling gas. There was never a long time lapse (more than a few hours) between adjusting the pH of the seawater and generating the aerosol sample from it.

The data resulting from the experiments of September 10 and September 20 are shown in Table 2. Since the data resulting from these two experiments are not of very good quality, and a pH effect was not evident, the analysis of variance technique was employed to see what might be safely concluded. Considering first September 20, if grouping of the data is made according to pH, a significant difference between means (of F factors for different pH values) does not exist even at the 50% confidence level for either Cu or Fe. If a grouping is according to carboy, the probability of a difference (between F factors coming from different carboys) is 75% for Fe and less than 50% for Cu. The total

Table 2 "pH Experiments"

		F Factor			F Factor	
Carboy	pH	Fe	Cu	pH	Fe	Cu
Experiment 1, September 10						
1	8.6	14±1	22±2	2.0	11±1	19±2
2	8.6	17±1	29±2	2.0	13±1	-
3	7.7	34±2	27±2	7.7	-	26±2
4	3.7	15±1	22±2	4.0	10±1	17±1
5	2.3	28±2	20±2	2.3	16±1	19±2
Experiment 2, September 20						
1	8.2	52±3	35±2	1.9	63±4	52±4
2	8.2	51±3	31±2	1.9	32±2	35±3
3	7.4	38±3	37±3	2.6	38±3	4[illegible]±3
4	7.4	-	27±2	2.6	33±2	51±4
5	7.1	37±2	37±3	7.1	45±3	44±3
Experiment 3, September 30						
1	8.2	27±2	31±2	1.5	18±1	29±1
2	8.2	44±1	41±3	1.5	40±1	42±3

amount of variation expressed as a percent of the grand mean (s_1/GM x 100%) is 19% for Cu and 25% for Fe. Looking at the results of September 10, grouping either by pH or carboy, a significant difference between means exists at the 90% level for both Cu and Fe. Probably the reason for the greater probabilities here is that for the September 10 series, both subsamples of the same pH were usually also drawn from the same carboy, thereby making both factors work together to manifest a difference between groups. The total variations of Cu and Fe on September 10 are 18% and 25% respectively; these are nearly the same as the variations on September 20. Putting together the results from both series, it is not possible to say whether pH or carboy is the main source of variance, but the combined results do not imply that pH is an important factor controlling the magnitude of F. In fact, the maximum variation that could be attributed to pH in these experiments is 46% for Fe and 20% for Cu; this is not much considering the wide range of pH. On September 30, a final short attempt to see a pH effect was made. These data are presented in Table 2 also. The results of September 30 show that fractionation still occurs, at pH = 1.5, and support the overall conclusion that the short term effect of pH on F is not large.

It was supposed that ultrafiltration would reduce the capacity of a seawater sample to produce trace metal enrichments if the fractionating species involved were larger than the effective cut-off of the membrane. Using the Amicon TCF-10 system (described in a later portion of the text), it was possible to divide a large sample of filtered tap seawater into retentate and ultrafiltrate portions. The retentate is water which passes over the membrane and is enriched in macrosolute species. The ultrafiltrate is water which passes through the membrane, thus being purified of entities larger than the membrane's effective cut-off. The UM-2 membrane used in this and subsequent experiments has a nominal pore size of about .001 µm which is equivalent to molecular weight of 1000. After about a week, enough seawater was processed by the system to enable two comparative bubble fractionation runs to be made. This was done on two separate occasions. The first batch was bubble fractionated on September 30 at a pH of 6.0 (acidification is necessary to prevent losses due to adsorption). The second batch, which was partitioned at pH = 1.8, was fractionated at the same pH on October 14. Air was used in this and all subsequent bubble fractionation experiments. The air supply is considered to be free from obvious organic contamination; the air compressor is an oil-less commercial model with graphite piston rings. Three consecutive 5 ml aerosol samples were collected from each run and analyzed by the usual techniques. The results are collected in Table 3.

The effect of passing seawater through the UM-2 membrane is readily apparent; for both batches and both metals the fractionation of the ultrafiltrate was substantially less than the retentate. The fact that the second batch fractionated less well than the first may be a long term pH effect or simply the difference between samples of sea-

Table 3 The Fractionation of Ultrafiltered and U-V Irradiated Seawater.

Batch 1, September 30, pH = 6.0

	Ultrafiltrate	Retentate
Iron	6.6 ± .5	21 ± 1.4
	3.1 ± .5	16 ± 1.2
	5.0 ± .6	16 ± 1.1
Copper	6.6 ± 1.2	20 ± 1.0
	4.0 ± 1.2	13 ± 1.0
	3.4 ± 1.3	8.2 ± .9

Batch 2, October 14, pH = 1.8

	Ultrafiltrate	Retentate
Iron	2.7 ± .4	6.9 ± .5
	2.2 ± .4	5.1 ± .5
	1.8 ± .4	3.7 ± .4
Copper	1.1 ± .3	10 ± .4
	1.1 ± .3	2.7 ± .3
	1.4 ± .3	2.1 ± .3

Batch 3, October 18, pH = 2.1

	Irradiated	Non-irradiated
Iron	4.3 ± .2	14 ± 1.6
	2.2 ± .2	11 ± 1.5
	1.7 ± .2	
Copper	0.9 ± .2	17 ± .4
	1.0 ± .2	8.0 ± .4
	0.7 ± .2	

water drawn from the tap at different times. The results of these two experiments are an indication that the agency responsible for trace metal fractionation can be removed by a .001 µm ultrafilter.

The use of high intensity u-v light to oxidize dissolved organic matter in seawater is a technique currently in vogue with oceanographers. Based on prior experience gained in the study of the iron complex in Nova Scotia brooks, it was thought that this technique might be effective in destroying transition metal-organic complexes in seawater. A single carboy of filtered tap seawater was acidified to pH = 2.1 and divided into halves. One half was irradiated in 200 ml quartz tubes for an hour at a time, and the other half not irradiated. The results of the fractionation runs on the irradiated and non-irradiated samples are given in Table 3. As before, several successive samples of the aerosol were analyzed to improve the accuracy of the result. The irradiated sample clearly shows reduced fractionation. This is an indication that the agency responsible for trace metal enrichment is indeed destroyed by high intensity u-v light.

The F factors of irradiated and ultrafiltered seawater are among the lowest observed in any of the experiments which used filtered tap seawater. In fact, Cu shows zero enrichment in the u-v irradiated sample and in the ultrafiltered sample of October 14. Comparably low F factors were obtained only after seawater had been bubbled continuously for many hours and more than 100 ml of aerosol had been collected. Therefore, the effect of ultrafiltration and u-v irradiation is real. The implications of these results are explored in detail later.

In the technique known as ion flotation, a metallic ion such as CrO_4^{2-} can be floated as an insoluble product with a suitable surfactant, e.g. a quarternary alkyl ammonium bromide. Since some form of ion flotation may be operating to produce observed enrichments of trace metals in seawater, it was considered important to investigate the effect of artificially added surfactants.

Early experience with the use of surfactants such as sodium lauryl sulfate indicated that the addition of a surfactant in minute quantity during a run improved aerosol formation and effected a slight elevation in the F factor. The data of October 6 illustrate what happened when first a small amount of sodium laurate and later the same dose of nor-leucine were added to the ultrafiltrate seawater of September 30 while bubbling was in progress. The initial enrichments seen in Table 4 were low and diminishing; F increased slightly after 10^{-6} M of sodium laurate was added, and more or less held constant after the introduction of nor-leucine. Sodium laurate also caused an increase in the rate of aerosol production; the droplets became finer and more prolific. By the time 15 ml of aerosol was collected, the surfactant was depleted; jet drop ejection was no longer vigorous, and bubble stabilization at the interface had begun to occur. If bubbling had continued, eventually a stable froth would have formed at the top of the column. As little as 10^{-8} M of sodium laurate would restimulate [illegible] 4 [illegible]

[illegible] - 7.0.

	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
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aerosol production; the change would be temporary but dramatic. Larger amounts of sodium laurate (5×10^{-6} M) do not augment the F factor any more than small amounts, but will cause a white precipitate on the surface of the collector, probably due to formation of the insoluble calcium and magnesium soaps. A milky opalescence can result when 10^{-7} M of Zephiran Chloride (alkyl dimethylbenzylammonium chloride) is used as a collector. Particle and micelle formation are sometimes also observed with natural seawater.

In order to see what effect if any the charge of the surfactant might have on fractionation, three trials were made from a 30 litre sample of filtered tap seawater on November 3. On the first trial, 1.5×10^{-7} M sodium lauryl sulfate (anionic surfactant) was added to the column of seawater before bubbling commenced. The same dose of the cationic Zephiran chloride was used for trial two; the third trial was without surfactant. Very small samples (100 µl) of aerosol were collected with a flat, level sheet of polyethylene film so that the maximum possible enrichments might be seen. The 100 ul aliquots of aerosol were added to 3 ml aliquots of original seawater in Quickfit tubes and extracted at constant volume and pH as before. The first four aerosol samples were consecutive; the last two were collected after an additional 1 ml.

The results presented in Table 5 do not indicate an augmentation as observed before, but rather a diminution of the F factor by both surfactants. Moreover, there seems to be no difference in effect between the anionic and cationic

Table 5 The Fractionation of Seawater Using Ionic Surfactants of Opposite Charge.

Sodium Lauryl Sulfate	Zephiran Chloride	NoSurfactant
	Copper	
39 ± 1.2	37 ± 1.2	61 ± 1.4
55 ± 1.4	38 ± 1.2	67 ± 1.6
29 ± 1.0	41 ± 1.2	72 ± 1.6
27 ± 1.0	45 ± 1.2	56 ± 1.4
26 ± 1.0	31 ± 1.0	20 ± .8
25 ± 1/0	37 ± 1.0	18 ± .8
	Iron	
33 ± 1.0	29 ± 1.0	53 ± 1.2
34 ± 1.0	30 ± 1.0	71 ± 1.4
30 ± 1.0	37 ± 1.0	64 ± 1.4
18 ± .8	31 ± 1.0	62 ± 1.4
22 ± .8	23 ± .8	24 ± .8
26 ± .8	29 ± 1.0	23 ± .8

surfactants. These apparently conflicting observations can be reconciled if the influence of artificial surfactants is the physical one of facilitating the ejection of jet droplets. The slight elevation of F seen in Table 4 is then explained by the production of smaller bubbles and hence, a thinner section of the interface being sampled. The initial supression seen in Table 5 could be due to competition with natural surfactants for the available surfaces. If artificial surfactants were chemically associated with trace metal species in seawater, the charge of the surfactant ions would be important. Finally, if the agents responsible for fractionation were simple surfactants, then the addition of artificial surfactants to natural seawater should result in aerosol enrichments comparable to those observed naturally. These arguments are expanded in relation to a model for trace metal fractionation to be developed later.

More evidence resulted from two minor experiments. A 19 litre carboy of artificial seawater (ASW) was made up for the purpose of running some bubble fractionation experiments; reagent grade salts and deionized water (Millipore "Super Q") were used in the recipe. Without prefiltering and without adding surfactants, it was found that the ASW produced enrichments of Fe that were quite high and that Cu fractionated well too. This was surprising since fractionable (surface active) species of trace metals were not expected to be present in ASW. In order to test the possibility that fractionation of Fe had been caused by particulate matter, the ASW was filtered and bubbled again. This time the fractionation of Fe was reduced and that of Cu was eliminated. The dissolved Fe concentration of the bulk seawater had also been largely removed. The yellowish precipitate collected on the filter was tested for Fe with thiocyanate. The test indicated that the material was probably $Fe(OH)_3$, supporting the hypothesis that fractionation in ASW was caused by precipitated $Fe(OH)_3$. This is in accordance with the earlier observation that ASW contains rather high concentrations of Fe (and other trace metals) which might be expected to precipitate during bubbling with air. As a precipitate, Fe can be removed by flotation (Rubin, 1972).

Partly in connection with the investigation of the estuarine fate of the organic complexes of Fe in Nova Scotia brooks, and partly for its relevance to the chemical fractionation of seawater in general, some bubbling experiments were made on mixtures of brookwater and seawater. Since these experiments were exploratory, only a brief discussion of some precursory indications is warranted. There were strong signs that the organic complex of Fe did fractionate. Aerosol enrichments similar to those observed in natural seawater could be effected in depleted seawater by the addition of a small amount of brookwater (20 ml). At least part of the enrichment of metal could be filtered from an aerosol sample. Furthermore, both Fe and natural fluorescence fractionated to approximately the same extent, implying that the metal and the fluorescent organic compounds from the brook might be associated. Final conclusions will be deferred until further work is done.

To gain further knowledge about the effect of ultrafiltration on the species composition, the partitioning of trace metals by ultrafiltration as a function of pH was investigated. The Amicon TCF-10 system in single pass mode is well suited to making quantitative measurements of the "ultrafilterability" of trace metals in seawater. The cell is constructed of polyethylene, polycarbonate, and Delrin. With the exception of Zn, experience has shown that contamination from the TCF-10 system is not detectable. The main advantage of single pass thin channel (TCF) systems over the conventional dead-end cell is that the sample is being continuously partitioned by the membrane at a constant volume ratio. This is important since the retention characteristics of a given membrane are sensitive to the volume concentration factor, V_o/V_r. Flow conditions, once established, can be maintained throughout a series of runs or reestablished later for further runs without loss of comparability. The retention efficiency changes during ultrafiltration in a dead-end cell, making quantitative measurement and interpretation more difficult. Since losses due to adsorption at higher pH become important, metal concentrations are measured in the original, retentate, and ultrafiltrate solutions and a budget is calculated routinely. To the extent that adsorption is indicated, the partition measurement is invalidated, because the loss cannot be correctly ascribed to either the ionic or colloidal fractions.

The experimental quantity that is derived when seawater is partitioned between retentate and ultrafiltrate is the retention coefficient, R, which is a characteristic of the membrane for a given macrosolute species. The retention coefficient is $R = \ln(C_r/C_o)/\ln(V_o/V_r)$, where the subscripts "o" and "r" refer to the original and retentate seawater samples, respectively. For material that is entirely excluded by the membrane, the retention coefficient is equal to one; for freely permeable ions and microsolute species, the value is zero. Since the diffusivity is both a function of the mean distribution of pore diameters and the size and shape of the molecules, the membrane cut-off is not sharp and well defined. This is particularly true for the unknown mixture of trace metal binding entities in natural seawater. Therefore, although a strict interpretation of molecular weight or the extent of metal binding is elusive, a relative number can be measured and related to some external variable such as pH.

Early experiments using deionized water solutions of trace metals in specified form uncovered some of the pitfalls of using ultrafiltration to infer speciation. For example, it was found that the EDTA complex of Fe was partially rejected by the UM-2 membrane even though the molecular weight is less than half the nominal cut-off. The dependence of R on flow conditions for Fe-EDTA was such that over a volume concentration factor increase of 327%, a 28% error would be incurred in the estimation of the solute concentration factor, if it were assumed that R remained constant over the interval. Since the volume ratio can be controlled or held constant to within a few percent, this needn't be a problem.

The data accumulated on the ultrafilterability of trace metals in seawater is a composite of several different experiments. Data were derived from the partitioning of large batches of seawater for the two bubble fractionation experiments at pH 6 and pH 1.8 (Sept. 30 and Oct. 14, Table 3). A series of partitionings of a single sample of tap seawater was made on Oct. 26 at pH values of 2.0, 2.4, 2.9, and 3.3. Finally, the u-v irradiated seawater used in the bubbling experiment of Oct. 14 was partitioned at the pH of 2.5. A minimum of 24 hours equilibration time was allowed after adjusting the pH for all samples. Extractions were made in duplicate from duplicate samples, and overall precision was quite good. The composite results are presented in Table 6.

Budgets were calculated for all metals at all pH values and were satisfactory with the exception of Zn, which showed a small amount of contamination from the cell. The coefficient of variation for the aggregate budget was 4%. Although retention coefficients have been translated into the per cent of metal retained ($100(2^R - 1)$), it cannot be assumed that this is exactly equal to the per cent of bound metal in equilibrium with free metal ions. In spite of the limitations already stressed, certain facts are open to clear interpretation. There definitely appears to be a measurable pH dependence of the per cent metal retained, which suggests that some sort of equilibrium exists between metal bound to the macrosolute moiety and metal ions which are free to pass the membrane. Also, the retention of Fe

Table 6 Ultrafiltration Partition Experiments. The values given are for the Retention coefficient with "Percent of metal retained" in parentheses.

Date	Oct. 13	Oct. 26				Oct. 15	Nov. 3*
pH	1.8	2.0	2.4	2.9	3.3	6.	2.5*
Iron	.11 (8)	<.05(<4)	.08 (6)	.12 (9)	.17(13)	.23(17)	.04 (3)
Copper	.18(13)	.18(13)	.27(21)	.29(22)	.34(27)	.60(52)	.10 (7)
Manganese	-	<.05(<4)	.09 (6)	.09 (6)	.05(<4)	-	-
Zinc	-	(< .15, contamination problem)				-	-

* U-V irradiated seawater, batch 2

and Cu in the u-v irradiated seawater is the lowest. The varying degrees to which different metals are held back suggests that the extent of involvement with a macrosolute species is different for each metal. Apparently Cu is considerably more associated with colloidal matter than is Fe. Both Cu and Fe retention are pH dependent. The very low retention coefficients and lack of ostensible pH dependence for Mn suggest that the extent of its involvement with colloidal matter is negligible.

To clarify the outcome of the various experiments, the following observations are recapitulated: Chemical fractionation of dissolved Cu and Fe in filtered seawater taken from the tap has been observed consistently. The measured enrichment is largest initially, decreases (probably exponentially) with time, and if bubbling were continued until enrichment diminished to zero, a substantial proportion of the original concentration would be lost to the aerosol. It was found that subjecting a sample of seawater to u-v light or forcing it through an ultrafilter reduces its ability to fractionate. Adding artificial surfactants to the seawater was observed to either enhance or suppress fractionation slightly. The presence of similar organic compounds in natural seawater is ruled out as a possible reason for fractionation of transition metals in seawater. Sizeable fractions of trace metals were retained by the UM-2 ultrafilter in the pH range 2 - 6. The retention of Cu was between 13% and 52%, and that of Fe was $< 4\%$ to 17%. Although lowering the pH a short while before the seawater is bubbled does not seem to affect the magnitude of F, R varies markedly with pH (R increases with increasing pH), when a longer period is allowed for equilibration. The sample of seawater which had been exposed to u-v light showed the least tendency to be affected by ultrafiltration.

The fact that chemical fractionation of certain transition metals occurs during the production of jet drops at the air/seawater interface is evidence of complexity in the chemical speciation of these elements. The major inorganic species that are postulated to exist in seawater, i.e. the hydroxy, chloro, sulfato, and carbonato complexes, are not fractionated, because they have a negligible potential for the air/seawater interface (MacIntyre, 1974a). Therefore, it is reasonable to insist that an association exists between metal species and some organic ligands which then promote adsorption of the associated metal to the bubble surfaces. The simplest model that can be proposed is that of counterion attachment of metal ions to an adsorbed monolayer of, for example, a fatty acid. This model is exemplified in studies of the foam separation of Cu^{2+} and Zn^{2+} with sodium lauryl sulfate at $pH \overset{\sim}{<} 7$ (Rubin, 1972). Removals of 100% can be achieved in distilled water, but decline at higher ionic strength because the interaction between collector and colligend is not specific. The observation that simple surfactants added to seawater have little effect on F can be rationalized by the extremely low association constant for the metal-surfactant complex formed. In seawater, counterions are predominantly Na^{+}, Ca^{2+}, and Mg^{2+}. Even the chelating amino acid nor-leucine did not cause fractionation at a concentration of 10^{-6} M. Therefore, it is necessary to discard the old model of Langmuir and Schaeffer (1937) when discussing trace metals in seawater, and postulate the presence of more powerful ligands.

In MacIntyre's early work on phosphate, he found that positive and negative surfactants played a vital role in distilled water solutions. At the ionic strength of seawater, however, competition with the main ionic species could completely alter the picture. The experiments of Van Grieken et al (1974) indicated that fractionation effects can be observed in seawater using radiotracers. The use of radiotracer elements to measure fractionation of trace elements in seawater in the laboratory should be approached with caution, however, since equilibrium between natural and radioactive species may not be attained and the observed F factor may be entirely different from that which occurs naturally.

In a generalized model of chemical fractionation at the air/sea interface, jet droplets are composed of the finite layer of water and adsorbed substances which actually constitutes the bubble surfaces. The main factors thought to be responsible for the magnitude of F are the following:

1) the activity of the species in solution, a;

2) the potential of the species to adsorb at the air/water interface and produce a surface excess concentration, G_s; (This is related to surface tension, γ, by the Gibbs equation, $G_s = \frac{1}{RT} \frac{\delta\gamma}{\delta \ln a}$.)

3) the mean size distribution of the bubbles, which determines the thickness of microlayer sampled, t;

4) the bubble age or path length;

5) the total composition of the solution, through possible competitive and cooperative effects; and

6) whether jet or film droplets are produced.

Since all of the above factors have not been investigated in the laboratory, what can be said about the magnitude of F in the environment? It is possible to arrive at a rough estimate of the maximum possible value of F for the fractionation of dissolved organic matter in the ocean by making a few reasonable assumptions. If the aerosol generated at the sea surface is restricted to jet drops, the bubble microtome principle of MacIntyre (1974a) probably applies and can be used to obtain a realistic estimate of the thickness of microlayer sampled, t. If then an upper bound for the surface excess concentration, G_s, of organic matter adsorbed to bubbles can be obtained, the volume excess concentration, G_v, can be calculated by the formula $G_v = G_s/a$. The fractionation factor F is simply, $(G_v + a)/a$. The surface tension measurements of Jarvis (1967) provide the information needed to derive an upper limit for the surface excess concentration of organics on bubbles. He found that the surface spreading pressure of natural films on freshly cleaned seawater develops slowly to a maximum of 0.1 dynes/cm after 20 minutes. This implies that films on rising bubbles probably do not develop past the gaseous or expanded phase, which sets an absolute minimum of 100 $Å^2$ per molecule for typical monolayer forming materials, e.g. lauric acid. If molecular areas are between 1000 and 100 Å^2, surface excess concentrations are in the neighborhood of 10^{-11} - 10^{-12} moles/cm^2. For average bubbles between 0.1 and 1.0 mm, the microlayer thickness is 10^{-5} - 10^{-4}cm. These figures combine to yield drop volume excess concentrations in the range of 10^{-7} - 10^{-5} moles/cm^3. Assuming 1 ppm of organic matter and an average molecular weight of 1000, seawater is 10^{-9} moles/cm^3 in organic carbon. Therefore, the most likely (mean) estimate for F_{max} is 10^3. This can be compared with the findings of Hoffman and Duce (1976b), who measured fractionation of total organic carbon in aerosol particles generated in the laboratory. Their enrichment values of 250 ± 145 for Narragansett Bay aerosols and 73 ± 27 for Sargasso Sea aerosols are certainly within the limit set by this calculation.

The thrust of the evidence accumulated has been to disclose that the fractionable metal species is larger than .001 µm (1000 molecular weight) and that this large molecule or colloid is broken into smaller units, or its ability to bind metals is destroyed, by u-v energy. Previous experience with the u-v apparatus indicated that one hour of exposure is sufficient to completely decolor yellow brookwater and remove interference to the thiocyanate test for Fe^{3+}, or to precipitate Fe(OH)$_3$ in culture media solutions containing Fe-EDTA. U-V energy is probably more efficacious in oxidizing transition metal complexes than dissolved organic compounds in general, because of the ubiquitous charge transfer absorption bands in the former (Zika, pers. comm.). The persistence of ultrafiltration and aerosol fractionation effects at $pH < 2$ after several days of equilibration argues against causation by hydroxy-colloids unless they are metastable. But the enriched species in retentate and aerosol is not inert, since it reacts readily with sodium diethyldithiocarbamate when it is solvent extracted. To suggest that metal-organic colloids would satisfy the observed behaviour is not unreasonable, considering that much of the sea's organic matter has not been chemically characterized and that colloidal-sized organic matter has been found in seawater (Ogura, 1974; Sharp, 1973).

Colloids and organic macromolecules usually display a preference for the air/water interface (Gaines, 1966). By controlling the ionization of functional groups, pH directly influences the surface activity of individual molecules. The size distribution of organics in seawater may also be influenced by pH through its effect on the aggregation of various molecules by ionic and hydrogen bond forces. (The concentration of organics in collected aerosols has sometimes been observed to exceed the critical micelle concentration.) For these reasons and because OH^- competes with organic ligands for metal ions, prediction of the effect of pH on the magnitude of F would not be straightforward.

The interpretation placed on ultrafiltration studies relies on the discrimination of the membrane being purely based on size. Previous experience with unbuffered (pH 5 - 6) deionized water solutions of trace metal ions indicated that strong adsorption made R difficult to interpret. The presence of adsorption can cause R to be greater than zero by Donnan exclusion. (According to Amicon literature the UM-2 has a low density of ionic sites and a net zero charge.) The addition of inert electrolyte or lowering the pH curbs this effect. There is no evidence that an ultrafilter would act as an ion-selective semi-permeable membrane. The techniques of ultrafiltration and dialysis have been used to determine the concentration of truly dissolved forms of trace elements in river and lake water (Benes and Steinnes, 1974).

The pronounced pH dependence of the ultrafilterability of Cu and Fe is what would be expected for metal binding to weak acid ligands. It could also be explained as the effect of pH dependence on the charge of a polyelectrolyte ligand, or perhaps it is a manifestation of the pH dependent aggregation of smaller molecules. If natural complexes are labile the equilibria can be studied further with metal ion buffers. The per cent of total metal that can be fractionated in an aerosol makes a better comparison to the per cent of total metal retained by an ultrafilter than does the F factor. Fractionation experiments indicate that at least 5 - 10% of Cu and Fe can be removed by bubbling.

Both aerosol fractionation and ultrafiltration have the disadvantage that the measured distribution between free and bound metal species is not necessarily the same as the equilibrium distribution of these species. The shift from true equilibrium would have to be inferred from a more complicated approach using these techniques. If perturbations are small, then it would appear that a substantial proportion of Cu and Fe (and perhaps some other metals) exist as bound colloidal species. The oceanographic variability would have to be examined before any kind of quantitative estimate could be made.

Owing to the competing effects of major ions in seawater, the existence of bound transition metal ions at pH 2 implies a strong specific interaction between the organic moiety and metal ion, probably chelation. This is certainly feasible for a combination such as Cu^{2+} and citrate ion, where as little as 10^{-7} M of the latter ties up a significant fraction of total Cu^{2+}, but many other possibilities exist. What kinds of organic molecules that are either known or expected to be present in seawater could fulfil this role? Much has been theorized though little is actually known about the full range of compounds that compose the dissolved organic carbon (DOC) of the ocean, so the discussion of this point is intended to be brief. Fulvic acid, a carboxylated, hydroxylated, somewhat polymerized aromatic structure is certainly a possibility. It posesses most of the qualities, such as polyfunctionality, that are presumed to be important, and it definitely binds transition metals in rivers and lakes. On the basis of IR spectra combined with surface tension and potential measurements, Baier et al (1974) have concluded that natural surface films and foams are dominated by proteoglycans and glycoproteins. Other possible substances in the ocean include polyphenolic compounds of marine origin, proteins and polypeptides, polycyclics such as cholesterol, vitamins, enzymes, porphyrins, and smaller molecules such as α-amino acids and α-hydroxy acids. This list is not complete and is only intended to show the likelihood of transition metal complexing agents in the ocean. The characterization of organic compounds which form ligands with transition metals in seawater would seem to be a fruitful area for further work.

Summary...

The chemical fractionation of dissolved Cu and Fe proceeds by the mechanism of adsorption of metal-binding colloids to rising bubbles and subsequent concentration of these species on jet drops which are ejected when bubbles rupture at the surface. The existence of a metal-organic colloid which sequesters a significant fraction of total Cu and Fe present has been inferred from the results of fractionation, u-v irradiation, and ultrafiltration experiments. Strong binding of the metal to the colloid is indicated by its persistence at low pH. Some kind of large molecular weight organic entity, perhaps a polymer, is conjectured.

Chemical Fractionation in the Context of the Air/Sea Interaction

The air/sea interaction is concerned with the transport of matter between the atmosphere and the surface layer of the ocean. The air/sea interaction cannot be considered exclusively; it is complicated by other interactions, e.g. continents/atmosphere, surface layer/deep ocean, troposphere/stratosphere, rivers/oceans, etc. It is obvious that the source of sea salt in the atmosphere is the sea, and that the continents supply the fine mineral matter called dust. But many other processes contribute to the nature of marine aerosols; a significant proportion originates from volcanic activity and combustion processes (not the least of which is anthropogenic). Gas reactions are another source of particles. Junge (1972), in his review of the present knowledge of aerosols in the undisturbed marine environment, distinguishes between the following five components: particles with radii larger than ~ 20 µm, sea spray particles, tropospheric background particles, mineral dust particles, and particles with radii smaller than ~.03 µm.

It has usually been the object of chemical investigations to relate apparent enrichments of certain elements in the marine atmosphere to processes occuring at the sea surface during the production of sea salt particles. Duce and Hoffman (1976) have considered the available evidence and concluded that the only cases where positive enrichments of more than a few per cent can be clearly ascribed to chemical fractionation at the sea surface are I, PO_4^{3-}, probably organic nitrogen and organic carbon, possibly some heavy metals, and possibly K in biologically productive waters. This is not to ignore other examples of fractionation which may be obscured by the presence of high concentrations in the atmosphere from other sources. Bubble scavenging and enrichment of PO_4^{3-} in laboratory aerosols have been attributed to associated organic matter. In the case of I, both organic matter and gaseous I released from the ocean surface are believed to be responsible for the observed enrichments in the marine atmosphere. Actual measured enrichments of PO_4^{3-} and I in the marine atmosphere (either in rain or aerosols) generally fall into the range of 10^2 - 10^3, although enrichments as high as 10^4 and as low as 10^1 have been reported for I. Extremely high enrichments, 10^4 - 10^6, have been noted for nitrogen in several samples of snow and rain which were believed to be representative of the undisturbed marine environment. These may be linked to the fact that there are definite enrichments (up to 50) in the sea surface microlayer, or there may be (possibly more likely) reactions of gases such as NO_2 and NH_3 with aerosol particles. Fractionation of organic nitrogen has not yet been studied in the laboratory as has I, PO_4^{3-}, and organic carbon. There is little doubt that organic carbon is fractionated in the production of sea salt particles since surface active organic matter (SAOM) is implied in nearly every case of chemical fractionation. By a thorough review of all of the (sometimes exotic) physicochemical theories that have been advanced to explain the phenomenon of chemical fractionation in the marine environment, MacIntyre (1974a, 1974b) showed that association with SAOM is the most plausible universal explanation. There may be some difficulty, however, in distinguishing between organic material derived from the bubble breaking process and that present in other components of the marine atmosphere. A number of heavy and transition elements have been found to be enriched relative to seawater in marine aerosols. The elements Al, Fe, Mn, Sc, Ce, Th, and

Co generally have crustal enrichment factors near to zero and so are derived from continental dust. The so-called anomalously enriched elements, which include V, Cr, Zn, Cu, Cd, Hg, Sb, As, Pb, and Se, are present at levels between 10 and 10^4 times that which can be accounted for by the crustal component. Whether some of these anomalous enrichments can be explained by chemical fractionation will be discussed later in the light of the experimental facts uncovered in this thesis.

In general, when a substance is fractionated during the production of sea salt particles, it would be expected for the same reasons to be enriched in the sea surface microlayer. Microlayer enrichments could also be atmospherically derived, but owing to the dynamic nature of the sea surface it is unlikely that this mechanism would be important in areas situated far from major sources of continental aerosols (Hoffman et al, 1974). In a chemical sense, there is no essential difference between the microlayer and the jet drops produced during bubble collapse. In a holistic sense, though, there are differences, and one must be careful in drawing inferences about fractionation based on sea surface microlayer information. Experimentally it is considerably easier to generate an aerosol sample in the laboratory than to use any of the cumbersome methods of sampling the sea surface microlayer.

The adsorption of organic solutes at the air/water interface is quite general; all organic molecules will adsorb to some degree. The homologous series from propionic to lauric acid, for example, covers a range of affinities for the air/water interface that spans one million, yet the least surface active example (propionic acid) will adsorb until it is 10 times more concentrated at the interface than in the solution subphase (Davies and Rideal, 1961). Most of the interest in the past has been focused on the hydrocarbon-type molecules (e.g. fatty acids, alcohols, and amines), but more recently some complex biological molecules have been studied (e.g. phospholipids, vitamins, steroids and other natural polycyclics, porphyrin compounds such as chlorophyll a, as well as proteins and polypeptides). All of the above mentioned compounds (except propionic acid) exhibit high affinity for the air/water interface. It is therefore natural to surmise that a variety of interesting organic compounds resulting from the degradation of living cellular material will have a high probability of being enriched in the sea surface microlayer and of undergoing sea-to-air fractionation. The likelihood for a specific compound depends upon the other compounds present, because complex interactions are possible in both phases. Our knowledge of the kinds of organic compounds which are injected into the atmosphere is rudimentary and must be improved if we are to understand the chemical fate of organic carbon in the ocean.

The evidence which can be brought to bear on this question is meagre. There seems to be a general agreement that lipids are to be found in the microlayer, but it cannot be taken for granted that this is the entire story. It has been established that organic nitrogen and phosphorus are also constituents. This and the fact that transition metals, notably Cu, are fractionated suggests the possibility that SAOM is rich in donor groups, e.g. N, P, O, I, and S, needed for inner-sphere (coordinative) transition metal complexes. The fatty substances are only capable of forming the weaker outer-sphere (electrostatic) complexes, and counterions would be predominantly alkali and alkaline earth metals. The IR spectra and other film property measurements of Baier et al (1974) are primary evidence for the existence of highly substituted polymeric structures similar to humic materials. The electrophoresis and other surface studies of Loeb and Niehof (1975) demonstrate the seawater presence of large organic molecules, anionic in charge, which adsorb tenaciously to particle surfaces modifying their charge, and which are destroyed by u-v photo-oxidation. Their results are also consistent with the interpretation that SAOM is composed of degraded proteinaceous materials. If, as it seems, lipids constitute only a small part of the SAOM and are effectively displaced by larger more complex molecules, then sea-to-air fractionation may be an important factor in determining the chemical fate of a variety of biogenic organic compounds in the sea.

As mentioned previously, the marine aerosol consists of several other components besides sea salt. On the basis of size distribution and other information gleaned from the literature, Junge (1972) offered an idealized plot of the size spectrum of the various components of the undisturbed marine aerosol which was intended to summarize the state of his knowledge at that time; this diagram is reproduced in Figure 1. Below line a is the sea salt component which is the major component in the lower troposphere over the oceans. Between line c and line a is the tropospheric background aerosol which is always superimposed on the sea salt component. Occasionally, large concentrations of continental dust can be discerned in the particle spectrum over the ocean, as when an air mass originates in a Sahara dust storm; this is represented by line e. The important feature to note is that both the continental and the ubiquitous background components can significantly affect the composition of the marine aerosol in the size range where aerosols are normally sampled for chemical analysis. The tropospheric background aerosol is apparently not very well understood, but it is uniformly distributed throughout 85% of the troposphere, and it appears to originate in the upper troposphere. The chemical composition of the background aerosol is obscure, but it is believed to contain a large amount of sulfate. The information contained in the diagram for particles below ~ 3 µm is tentative and uncertain, especially with regard to the lower size limit for sea salt aerosols, which is thought to be between 1. and .1 µm. There is considerable uncertainty also about the relative contribution of jet and film drops to the sea salt spectrum. Woodcock (1972) suggested that a zone of transition between jet and bubble film source for Hawaiian marine aerosols occurs in the neighborhood of .2 - .4 µm. The residence time of sea salt particles over the ocean is not very much affected by particle size ac-

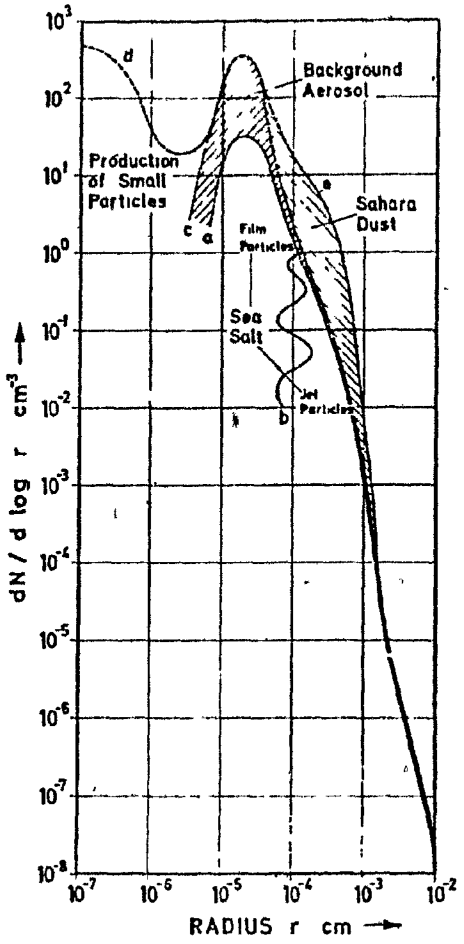


Figure 1 An idealized diagram of the various components of the undisturbed marine aerosol. From Junge (1972).

cording to Junge, since rainout and washout are considered to be the controlling factors. He estimated an average lifetime of about 3 days for particles smaller than 10 µm. This is probably non inconsistant with the corresponding value of one week for tropospheric aerosols over continental areas (Martell and Moore, 1974), if rainout and washout are expected to be more effective over the sea.

Within limitations, particle size spectra and other measurements of physical properties are useful sources of information in constructing a picture of the air/sea interaction, but the most conclusive data should come from chemical analysis, preferably in size fractionated aerosols. It would seem very desireable therefore to have chemical data on the tropospheric background aerosol. This could presumably be obtained at altitudes above 2 - 3 km over the oceans, where very little sea salt would be encountered.

Blanchard (1975) has written a succinct summary of his knowledge of the dynamics of sea spray formation; this is paraphrased below. Breaking waves, which begin to appear at 3 - 4 m/s wind speed, are the major source of bubbles in the ocean. Blanchard has observed concentrations of 10^8 bubbles per m^3 in the wake of whitecaps. Bubbles produced in this way range from < 100 µm to several mm in diameter, the size distribution being strongly inverse. The average bubble rises for 30 - 60 seconds before reaching the surface, but it is not stated how deep they may go. The adsorption of SAOM produces a negative charge on bubbles which probably results in their repulsion and non-coalescence. Very small bubbles ~~will~~ go into solution because of a pressure increase caused by surface curvature, leaving particles (which are presumably also negatively charged) (Johnson, 1976). If a bubble reaches the surface before going into solution it will burst with the ejection of jet drops or film drops or both depending on its size and the adsorption of SAOM. The height to which a jet drop rises is precisely a function of the diameter of the preceeding bubble, because the kinetic energy of ejection is derived from the surface free energy of the bubble. During the rise and concurrent adsorption of SAOM however, the surface energy of the bubble is lowered. This ageing effect on jet drop ejection height is pronounced and seems to attain steady state within 20 seconds. Blanchard found that film drops can be produced for bubbles larger than 300 µm. The number of film droplets increases rapidly with bubble size, and is also enhanced by clustering at the interface. Although a precise transition cannot be defined, most film droplets are in the < 1 µm category. MacIntyre (1974b) suggested a mechanism for chemical fractionation in film drops, but this has not yet been experimentally verified.

Despite the wealth of information on the physics of bubble bursting, the mechanism by which the ejecta receive organic enrichment has received insufficient attention. There hasn't even been an in-depth study of the physico-chemistry of the bubble microtome. This of course is an obvious practical approach to the dilemma of relating atmospheric enrichments to processes occuring at the sea surface. The bubble ageing effect on height of jet drop ejection, for example, might be directly related to the fractionation factor of organic carbon, but this has been overlooked. As has been demonstrated by film pressure and surface potential measurements, the adsorption of organic matter is both quantitatively and qualitatively affected by time. Because of the competitive nature of adsorption, F_{max} for specific compounds may exceed or fall short of F_{max} calculated or measured for total organic carbon. In assessing the sea as a source of various elements, e.g. P, N, and I, in the atmosphere, it would be helpful to know the F factors for each organic carrier. It should be feasible to obtain information on the potential for fractionation of various classes of organic compounds in laboratory experiments by adding trace amounts of radioactive compounds to natural seawater, generating aerosol particles, and measuring the resulting enrichments. This should be aimed at elucidating the physical-chemical mechanisms involved in film drop and jet drop fractionation. By simulating various bubble breaking conditions, such as bubble size, age, and clustering, wind speed, and type of seawater, the important mechanisms could be identified and extrapolated to the environment.

In order to evaluate the effect of chemical fractionation of transition metals on the marine atmosphere, Cu is chosen as an example since, of the four metals studied in the natural samples, Cu showed the greatest potential for sea-to-air fractionation. Cu is also an element which is known to be moderately enriched in the marine atmosphere. The major part of Cu enrichment on sea salt aerosols will probably come from the organic Cu colloid. This can be demonstrated by extending the St. Margaret's Bay observations to the oceans in general. Taking the observed mean value of 30 for F(dissolved) and the observed concentration range of 100 - 300 ng/l in surface waters, the resultant concentration of organic Cu in aerosol droplets is 3. - 9. µg/l. Assuming that particulate Cu is fractionated to the same extent as the other metals, F(particulate) = 200, and adopting Wallace, Hoffman, and Duce's (1976) range for particulate Cu concentration in surface waters, 1 - 10 ng/l, the expected contribution of particulate Cu is 0.2 - 2. µg/l. Therefore dissolved Cu should be between 60 - 98% of total fractionated Cu, if the data and assumptions are correct.

It may be premature to extrapolate from the values of F obtained by these experiments to the real situation at sea where physical conditions are infinitely more varied. For example, the entire spectrum of conditions under which aerosol droplets are formed was not investigated in the laboratory, and the fractionation of open ocean seawater was not measured. Nevertheless, even when ample allowance is made for under-estimation of F, it is rather unlikely that chemical fractionation is of sufficient magnitude to account for observed concentrations of Cu in the marine atmosphere. The maximum value of F observed for Cu in a fractionation experiment was $10^{1.9}$. Measurements of ambient aerosols at Hawaii, the South Pole, and Bermuda place the apparent enrichment of Cu relative to Na in the marine atmosphere into the range $10^{3.3}$ - $10^{6.0}$ (Hoffman et al, 1972; Zoller et al, 1974; Duce et al, 1976). This may not be a satisfactory comparison, since aerosols produced by the bubbling column are not entirely representative of those produced at sea in that the bubbles used in generating laboratory aerosols had an average diameter of about 1 mm. Bubbles of that size result in jet drops about 100 μm in diameter or salt particles of about 35 μm under average atmospheric conditions. This is near the upper limit for sea salt particles in the atmosphere. Therefore, laboratory F values will have to be revised upward to represent the entire spectrum of sea salt aerosols. The enrichments for smaller bubbles can be predicted by the bubble microtome principle. If the mean value of $10^{1.5}$ is accepted as the average F factor for 1 mm bubbles, the enrichments for 0.1 abd .01 mm bubbles are $10^{2.5}$ and $10^{3.5}$, respectively. These derived F values can be compared with those actually measured in size fractionated aerosols collected from a tower on the coast of Bermuda (Duce et al, 1976). The five stage impactor sampled the size range from > 3.6 um to < .25 μm. Enrichment factors, referenced to Na, were seen to increase with decreasing particle size, spanning the range $10^{5.8}$ - $10^{8.0}$. This is 3 - 4 orders of magnitude greater than that which could possibly be produced by the bubble microtoming of jet droplets into the atmosphere. Also the rate of increase of F with decreasing particle diameter in Bermuda aerosols is greater than that predicted by the organic film hypothesis, which indicates that F should vary inversely as the first power of the bubble diameter. This relationship was obeyed by organic iodine in the laboratory fractionation experiments of Seto and Duce (1972). The use of the bubble microtome principle is probably valid to explain fractionation behaviour in sea salt particles greater than .2 - .4 μm (bubble diameter > 10 μm). Woodcock (1972) believes that film droplets predominate below this range, however. Therefore, in order for sea-to-air fractionation to be a viable hypothesis, there must be a reasonable way to explain several orders of magnitude disparity between the laboratory F factor and the apparent F factor in the environment.

Turning from the hypothesis of sea-to-air fractionation, what else can be invoked to explain the anomalously high concentrations of heavy metals in the marine atmosphere? Duce et al (1975) have suggested that due to the relatively high volatility of some of these elements (As, Se, Pb, Sb, and Cd), a vapour phase may be important at the source. The anomalous elements tend to be more concentrated on the smallest particles, while the opposite is true for the crustal and sea salt elements. This is further evidence in favour of a vapour source (Duce et al, 1976). By now it is already fairly well established that these anomalous enrichments are a universal phenomenon which is found in diverse environments -- urban and rural, land and sea, Northern and Southern Hemispheres (Pierson et al, 1974; Zoller et al, 1974; Duce et al, 1975; Rahn, 1975). Though absolute levels vary greatly, being lowest in the remotest areas, the pattern of enrichments is always repeated. Continental dust is ubiquitous in the marine atmosphere, so it sould not be surprising that this finer component bearing high levels of rare elements is to be found there too. All of these facts are consistent with the idea that these anomalous enrichments are probably part of the tropospheric background aerosol. The sources of the background are probably many and varied, e.g. cosmic, fossil fuel combustion, smelting and other industrial activities, volcanoes, forest fires, etc. If the anomalous elements originate as a vapour or as Aitken particles ($< .1$ µm), then their presence in chemically analyzed aerosols might be the result of condensation, agglomeration, and other processes which contribute to the gradual shift up the particle spectrum. Hidy (1973) has shown that different removal mechanisms predominate in different size ranges, and that there should be subsequent differences in residence times. This fact should be considered when attempts are made to explain the steady state concentrations and distributions of elements associated with sea salt, crustal, and high temperature sources.

From the foregoing it is apparent that for most trace metals in the ocean, the atmosphere is a source rather than a sink. Cambray et al (1975) have estimated the input of trace metals from the atmosphere into the North Sea, and Duce and Hoffman (1976) have estimated the input of anthropogenic vanadium into a section of the North Atlantic Ocean. To further underscore this point, a table has been prepared (Table 8, Appendix) in which global trace metal fluxes from the atmosphere are compared with those from the world's rivers. Fluxes have also been estimated for the removal of the elements from the ocean by phytoplankton uptake. Since atmospheric concentrations vary tremendously geographically (Duce, pers. comm., 1977), it is not valid to take one region as representative of the global marine atmosphere. It is probably not valid either to assume that global fluxes based on river input or on sedimentation are applicable to a specific oceanic region. Furthermore, these global estimates are uncertain because of difficulties inherent in obtaining world average values, e.g. sediment composition and deposition rate vary geographically. It is not surprising that parallel estimates of weathering based on river input and sediment output do not agree. Therefore, the numbers in Table 8 should be regarded as order-of-magnitude estimates at best, and the table itself should not be taken too literally. Despite the crudity of this approach, these data do suggest that the atmosphere is a potent source of some transition and heavy elements in the marine environment. This is particularly true for the anomalously enriched elements. In assessing the impact of the atmospheric burden of anomalously enriched elements, total deposition velocities must be accurately determined for each element in the marine environment. There seems to be considerable uncertainty about the relative importance of dry deposition and rainout as well as the relationship between particle size and dry deposition velocity. Cawse (1974) has measured both dry fallout and air concentrations with an impactor at the same urban sites and has found a direct relationship between average dry deposition velocity and mass median diameter. At a typical urban location the highly enriched elements, Se, As, Sb, and Pb, had dry deposition velocities in the range 0.1 - 0.3 cm/sec while Fe and Al fell out at the rate of 1.1 - 1.4 cm/sec. In the absence of precipitation, dry deposition velocities are inversely related to atmospheric residence times. Thus, in order to maintain an enrichment factor of 1000, the anomalous elements must be injected and removed about 100 times faster than the crustal elements. On the other hand, if precipitation is much more effective than dry fallout, the relative flux could be a factor of ten higher. In order to clear up this uncertainty, it would be desirable to determine empirically the effective total deposition velocity for each element in the geographic region of interest. Finally, the solubility of the elements must be known to calculate their geochemical fluxes. The data of Cawse (1974) indicate that this is high (50 - 90%) for most elements; even Al, Sc, and Fe are soluble to some extent (10 - 20%). The implications of the atmosphere being the principal mode for some elements are that concentration profiles may be different for these elements and that input is geographically more uniform. The implications of the source function being anthropogenic are non-steady state concentrations and ecological changes. The fact that trace elements are cycled rapidly by plankton tends to keep the oceans in balance.

Before relegating chemical fractionation of transition metals to oblivion for its apparent inability to explain the anomalously high concentrations of heavy metals in the marine atmosphere, it should be remembered that fractionation is still an important aspect of the marine chemistry of the materials involved. Blanchard (1975) estimated that the sea/air cycling of SAOM amounts to 5 - 12% of the total yearly production of organic carbon in the ocean. This estimate may be too high since it was based on atmospheric concentrations of organic carbon rather than known potential for fractionation, i.e. the F factor for organic carbon. A more conservative estimate can be obtained by adopting the previously calculated F_{max} for organic carbon as an average figure for the oceans. This agrees with the average organic carbon/salt ratio of .05 observed in Bermuda by Hoffman and Duce (1976a). If the total transport of sea salt into the air is 10^{9} - 10^{10} tons/year, this puts the transport of organic carbon somewhere between 0.1 - 1.0 per cent of yearly production. Interestingly, if the same kind of calculation is repeated for Cu, assuming $F_{ave} = 10^{2.5}$ which seems reasonable, and basing the average concentration of Cu in phytoplankton on the analyses of Martin and Knauer (1973), one obtains the same numerical result. Because the assumption that F equals $10^{2.5}$ is not supported by an adequate investigation of oceanographic variability, however, this result cannot be taken seriously. The importance of the sea/air cycling of organic Cu can perhaps be best illustrated in another way. Consider the process of cycling through the atmosphere as a mechanism for exposing enriched sea salts to a unique chemical environment. Some of the attributes of this environment are high ionic strength (essentially saturated with respect to sea salt), low pH (the pH of cloud water is 5 - 6), and high flux of sunlight (sea surface value). This is actually a heterogenous chemical system where reactions in both gas and liquid phases are possible. Photochemical reactions would be expected to play a determining role, especially for transition metal-organic complexes. Organic compounds in general would probably tend to oxidize and volatilize, but how effectively in relation to similar reactions which occur in the photic zone? Cycling of SAOM through the atmosphere is almost certain to cause compositional changes, but what these are and how they fit into the organic chemistry of the oceans remains to be seen.

II. Trace Metal Patterns in the Gulf of St. Lawrence

The Gulf of St. Lawrence is an inland sea and a giant estuary, both aspects of which are pertinent to the study of trace metal distributions in the Gulf. The reader is referred for general information about the physical, biological, geological, and chemical environment to several current articles and reviews (Steven, 1974; El Sabh, 1976; Loring and Nota, 1973; Khalil and Arnac, 1975). This study examines the geographic dispositions of several transition metals in surface waters of the Gulf with the aim of discovering the important factors controlling the distributions and in particular of determining whether biological production has any discernable influence.

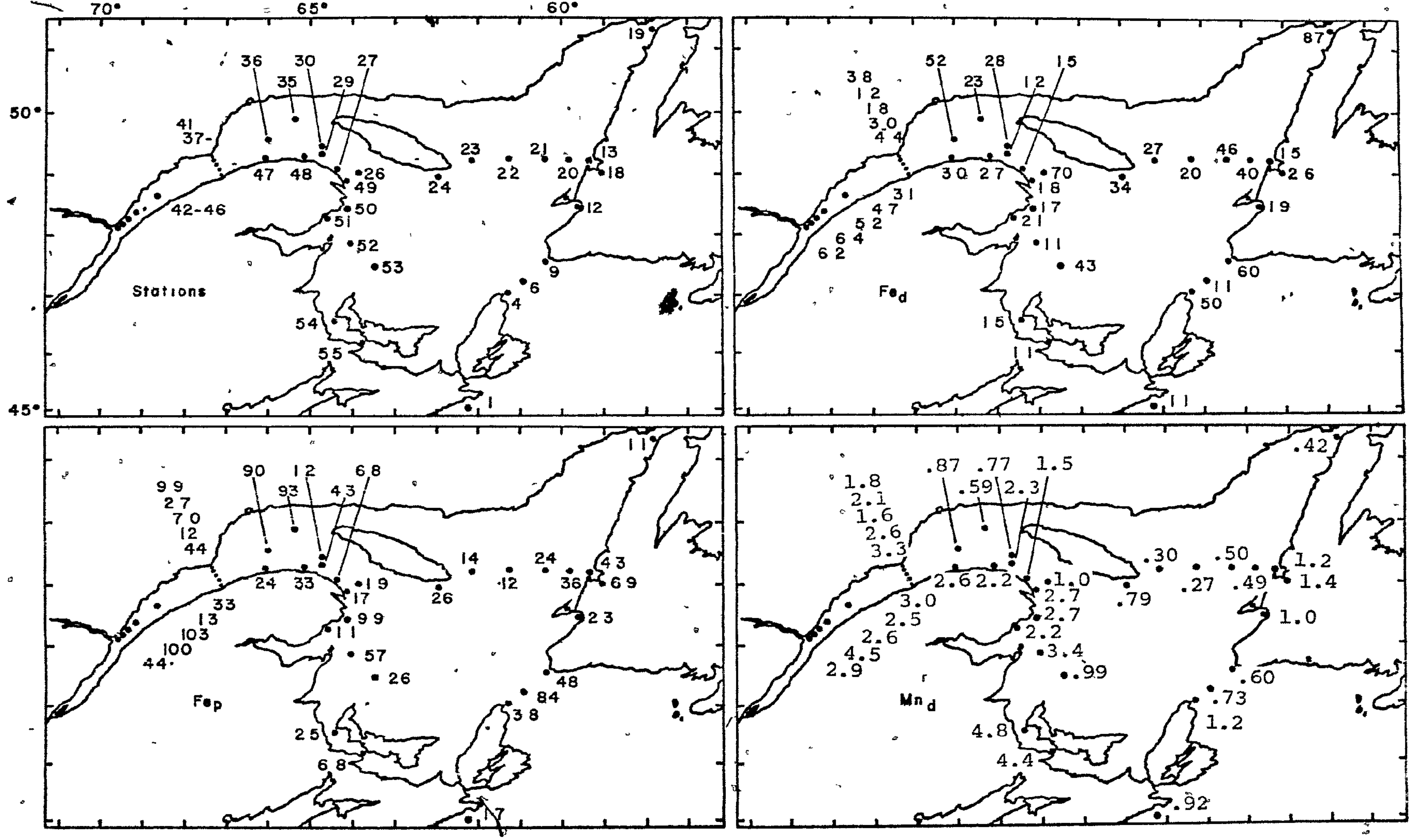
Although there has been much conjecture about chemical and biological interactions involving certain trace metals, direct evidence for the nonconservative distribution of these elements in the ocean is hard to find. Boyle and Edmond (1975) demonstrated that dissolved copper is enriched in surface waters of the Antarctic upwelling area relative to lower latitudes, and that copper covaries linearly with nitrate in these waters. Data from the present study are used to test the hypothesis that Fe, Mn, Cu, and Zn are enriched by nutrient recycling in the St. Lawrence Estuary. Spencer and Sachs (1970) showed with respect to Al, Fe, Cu, Mn, and Zn that suspended particulate matter in the Gulf of Maine reflects differences in elemental composition which are correlated with the presence of resuspended clays in deep water and phytoplankton in surface water. In particular, Fe and Al adhered to the disposition of suspended clays in deep waters while Cu and Zn were augmented by the presence of phytoplankton in surface waters. The distributions of particulate Fe, Mn, and Zn in the Gulf of St. Lawrence are interpreted by analyzing interelemental covariations in the light of the known physical and biological oceanographic features of the Gulf.

Surface samples were collected from 2 - 3 metres depth at 38 stations in the Gulf of St. Lawrence between May 27 and June 8, 1975 (BIO cruise 75-015). The stations sampled are seen in Figure 2. The nutrients nitrate, silicate, and phosphate were determined aboard ship by autoanalyzer. The sampling procedure consisted of casting a polyethylene jerry can from the bow of the ship immediately after coasting to a stop. The five litre sample was then filtered in an enclosed polyethylene system under ten pounds pressure through a 25 mm 0.4 µm Nuclepore filter. The first 500 ml of seawater was retained in an acid-cleaned polyethylene bottle and acidified to pH 3 with one ml of 1.5 N Aristar HCl. The filter obtained was dried at 60° C and stored in a glassine envelope. All of the seawater samples were analyzed within a month after the cruise. The analytical techniques used to determine dissolved and particulate trace metals are described in the Appendix.

The Dissolved Trace Metals

The dominant influence of the St. Lawrence River as a source of dissolved metals in the Gulf can be visually

Figure 2 depicts the stations sampled and the measured concentrations of dissolved Fe, particulate Fe, and dissolved Mn in the Gulf of St. Lawrence. Concentrations are µg/l.



appreciated by looking at the maps of dissolved Fe and Mn reproduced in Figure 2. That the same pattern is followed by Cu and Zn can be verified by referring to the station map of Figure 2 and the tabular data of Table 9 in the Appendix. The effects of tributaries are most apparent in the distributions of dissolved and particulate iron. High iron concentrations, for example, occur at inlets along the western coast of Newfoundland. On the basis of salinity, nutrient, and trace metal distributions the Gulf can be divided into two principal regions, these being the estuary and the open gulf. For the purpose of this discussion the estuary consists of the Lower Estuary plus the Gaspé Current and is represented by stations 37 - 50. The open gulf is a region which is remote from the influence of the estuary or other immediate influence of land. The stations which are representative of the open gulf are 20 - 24. In the estuary, where salinity ranges from 20‰ to 30‰, very high values of dissolved and particulate trace metals, nitrate, and silicate are found. The open gulf is c[illegible]acterized by much lower levels of dissolved and particulate trace metals, and nutrients are essentially zero. The scarcity of nutrient elements in surface waters of the maritime portion of the Gulf (excluding stations 37 - 50) indicate that at the time of the cruise the Gulf was past the season of active phytoplankton growth.

Overall variability of dissolved metals decreases in the order Fe > Mn > Zn > Cu. This sequence might be expected to reflect the relative differences in concentration between river water and seawater. Trace metal data on the St. Lawrence River is sparse but concordant with this assumption (Livingstone, 1963). The absolute levels of Fe, Mn, Cu, and Zn are very similar to those reported by Preston (1975) for British coastal waters. They are somewhat lower than those reported by Bewers et al (1974) in a previous study of the Gulf, probably owing to improved detection limits achieved with the graphite analyzer used in this study. There is no obvious evidence that the waters of the Gulf are polluted with respect to any of these metals.

At first sight, the regressions formed between the dissolved metals and salinity, shown in Figure 3, suggest that most of the overall variability is caused by simple mixing of fresh and saline waters in the Gulf. Accordingly, the order of decreasing r^2 for the regressions is the same as that of decreasing overall variability. The unexpectedly faithful correlation with salinity exhibited by dissolved Fe suggests that Fe is in effect a fairly conservative tracer of fresh water input into the Gulf over the range of salinities encountered. Considering the analytical uncertainties (see Appendix), it is apparent that simple mixing of two water masses does not explain all of the variability of these four metals in the Gulf of St. Lawrence.

By contrast, the distribution of nitrate and silicate in surface waters shows abrupt changes in the estuary which do not correlate well with the salinity gradients. The mechanism of nutrient supply in the St. Lawrence estuary is by vertical mixing and upwelling followed by horizontal trans-

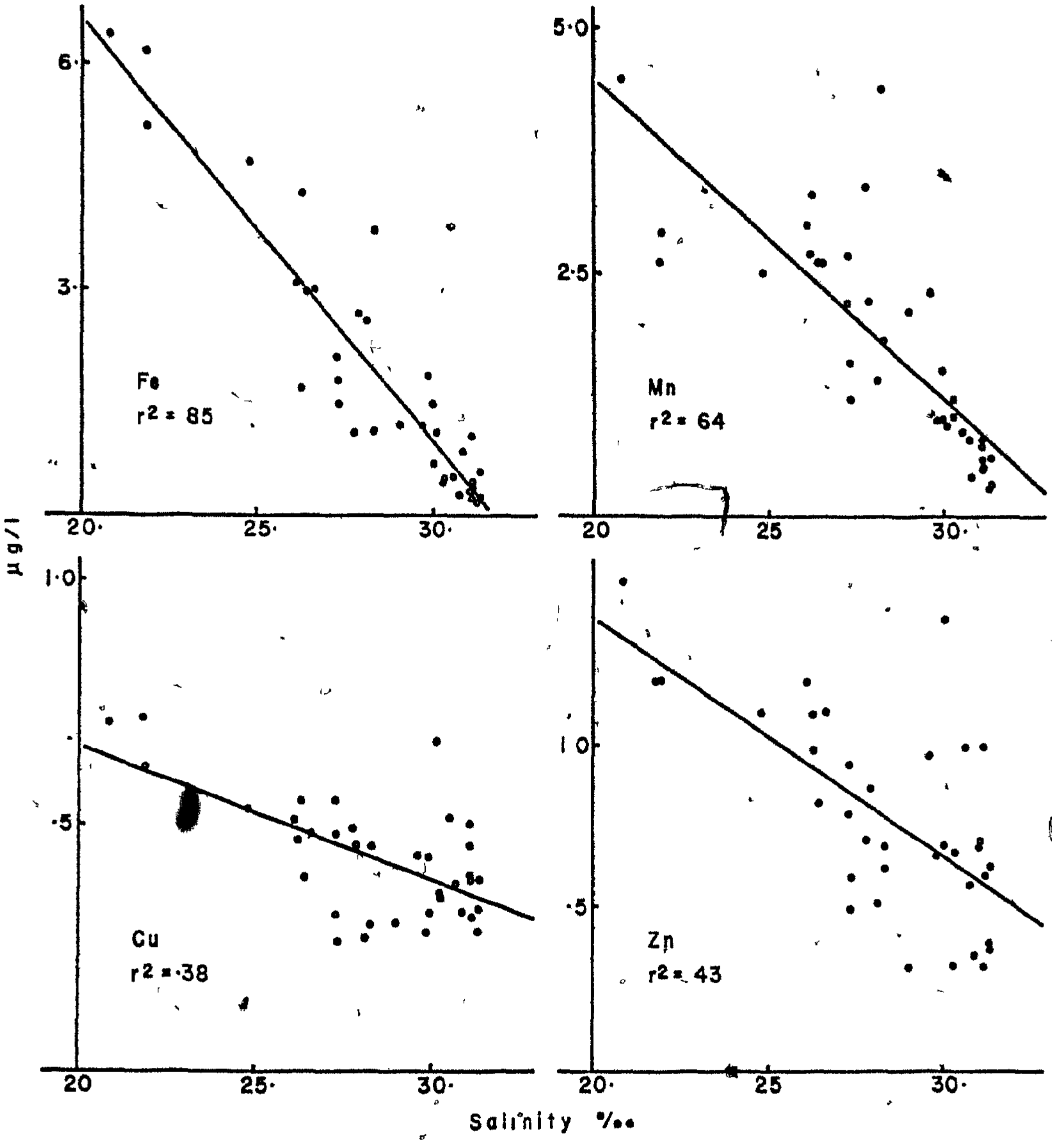


Figure 3 Graphs of dissolved transition metals versus salinity in the Gulf of St. Lawrence. The regression lines and correlation coefficients are based on all of the data points.

port in the eastward flowing Gaspé Current (Steven, 1974). The stepped concentrations seen in Figure 4 are thus attributed to the upwelling of nutrient rich subsurface waters caused by the estuarine circulation. Both fresh and deep water sources can be discerned for silicate, since stations 42 - 46 show a slight negative salinity dependence. The slope of the dependence implies that at the lowest salinity encountered, fresh water accounts for about 36% of the enrichment of silicate. Upwelling appears to be the predominant source for nitrate, however.

Given the existence of upwelling and nutrient intensification, it is relevant to ask whether trace metals considered to be essential for phytoplankton growth can be influenced by this process. It is recognized that trace metals may be controlled by both conservative (fresh water source) and nonconservative (in this case biological) processes. Therefore, there is a logical basis for comparing dissolved trace metals with salinity and nitrate. If the metal variations closely follow those of salinity, then the metal is considered to behave conservatively. If the relationship with salinity is not linear, but the metal also has a significant correlation with nitrate, then there is reason to believe that the concentration of the metal is controlled by both conservative and biological mechanisms. To investigate this possibility, data from the estuary were used to form linear regressions relating the dissolved trace metals to salinity and to salinity plus nitrate. The strength of each regression was evaluated by computing the appropriate

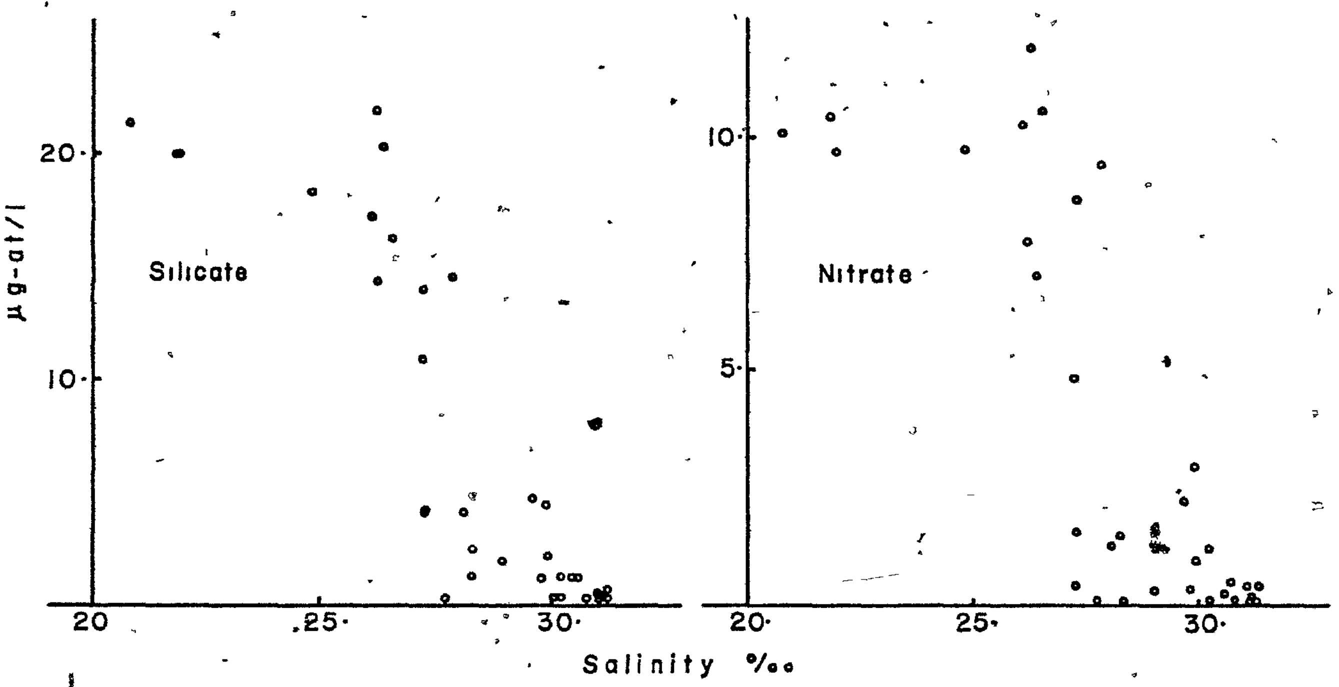


Figure 4 Dissolved silicate and dissolved nitrate versus salinity diagrams for the Gulf of St. Lawrence.

F ratio. Then to test the hypothesis that the regression on both variables results in a significantly better fit than the regression on salinity alone, a third likelihood ratio was computed by the methods of Brownlee (1965).

As can be seen from Table 7, the improvement brought about when both nitrate and salinity are invoked to explain the variation is very significant for Zn, Cu, and Mn, but not significant for Fe. There is a 99.9% probability that nitrate and salinity jointly account for the behaviour of Zn more completely than does salinity alone. The inference is thus that Zn, Cu, and Mn are not wholly conservative in the estuary, i.e. that they are enriched by the nutrient pump effect. This implies also that their concentrations are higher in the deep water entrained by the surface outflow. Lower significance for Mn in both regressions may mean that other factors are involved, such as adsorption or precipitation. The test employed is not an absolute criterion for nonconservative behaviour, because the extent to which covariation with nitrate is evident will depend on the relative importance of salinity. For Fe, the magnitude of the fresh water source may effectively mask the effects of a deep water one.

The coherent clustering of points for salinity greater than 30‰ in the scatter diagrams of Fe and Mn suggests that efficient mechanisms are operating to remove these metals from surface waters of the open gulf. It is expected that biological removal would be particularly important for both Fe and Mn (see "Trace Metal Observations in St. Margaret's

Table 7 Application of the analysis of variance technique to linear regressions relating the dissolved metals to salinity and nitrate. The data subset used consists of estuarine stations 37 - 50.

Metal	Hypothesis	r^2	F	Significance Level
Iron	a	.84	58.70	99.9%
	b	.87	34.42	99.9%
	c		2.44	75.0%
Manganese	a	.47	9.68	99.0%
	b	.74	13.94	99.5%
	c		10.41	99.0%
Copper	a	.81	45.75	99.9%
	b	.93	70.67	99.9%
	c		19.31	99.5%
Zinc	a	.62	17.91	99.5%
	b	.92	59.85	99.9%
	c		39.38	99.9%

a - Linear regression of dissolved metal on salinity

b - Linear regression of dissolved metal on both salinity and nitrate

c - Hypothesis that b yields a significantly better fit to the data than a

Bay"). It can be seen in the maps of dissolved Fe and Mn (Figure 2) that a definite depression in the concentrations of these metals exists in the waters of the open gulf. Comparison of the maps of Fe and Mn with the map of surface currents in the Gulf during June (Figure 5) reveals that the depression is situated in the area which is occupied by "a large permanent anti-clockwise gyre present during the ice-free months of the year" (El Sabh, 1976). The depressions may thus be due to the relative isolation of waters involved in the circulation of the gyre and the removal of dissolved trace metals by biological production.

That a sink for dissolved Fe and Mn does indeed exist in the open gulf can be demonstrated in another way. The regressions of Figure 3 indicate that Fe and Mn are removed faster than they are diluted, because these curves extrapolate to zero concentration before the salinity of the open ocean is reached. In other words, these curves imply that the concentrations of Fe and Mn in surface waters of the open ocean are -1.8 ± 1.3 and -0.4 ± 1.3 μg/l, respectively. The first impression created by Figure 3, that Fe is a fairly conservative tracer in the gulf was thus an illusion. The non-linearity of Mn vs salinity is less deceptive. Clearly, Fe and Mn are removed from the open gulf faster than these waters can exchange with the water outside the gulf. Since the mean flushing time of the Gulf of St. Lawrence is between 200 and 510 days (Steven, 1974), the rate of nonconservative removal of these metals is quite fast.

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The large scatter at high salinity in the diagrams of

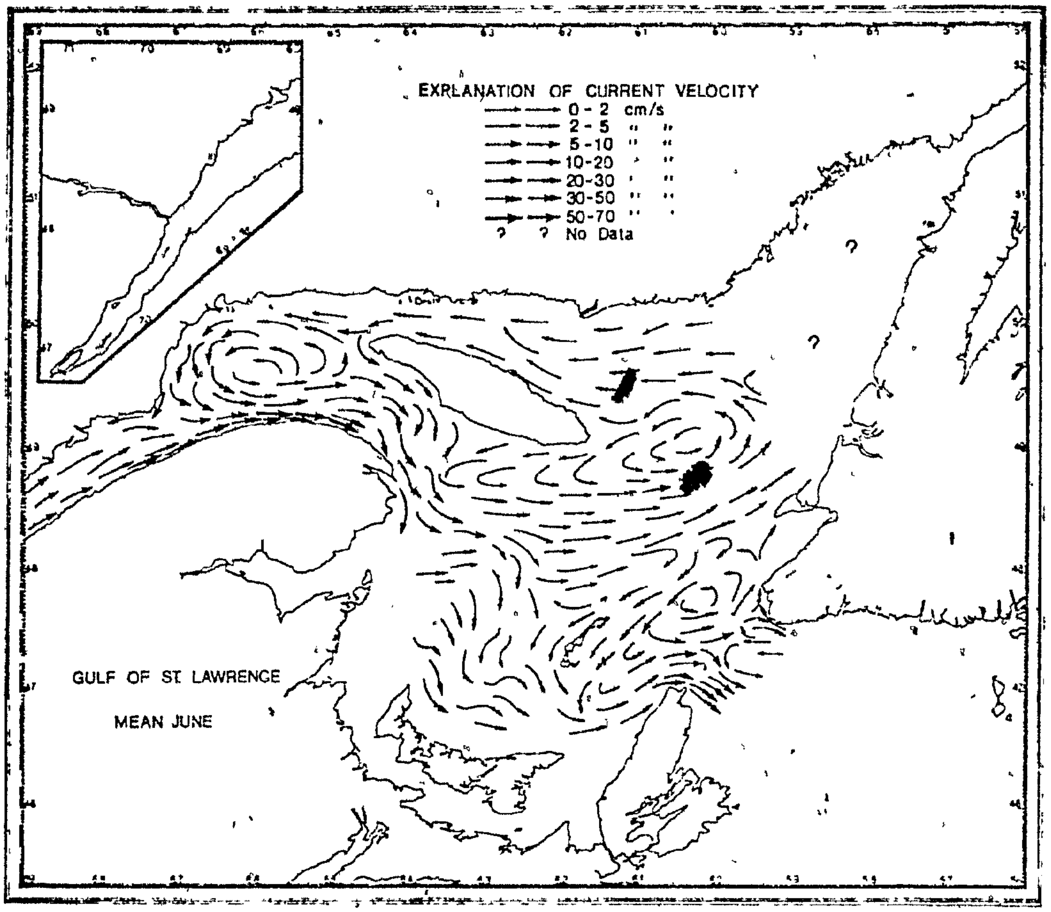

Figure 5 Field of the surface geostrophic currents in the Gulf of St. Lawrence during June. From El Sabh (1976).

Cu and Zn suggests that scavenging is relatively inefficient for these metals or that there are unidentified sources. By contrast with Fe and Mn, the concentrations of Cu and Zn are not conspicuously lower in the open gulf. Since the variations of Cu and Zn at high salinity do not correlate with NO_3, a possible source of Cu and Zn could be the atmosphere (see "Chemical Fractionation of Dissolved Transition Metals"). The possibility of contamination cannot be ruled out for Cu and Zn, however.

The Particulate Trace Metals.

The geographic distribution of particulate trace metals in the Gulf can be represented by a map of particulate iron, Figure 2. The common features of the distribution of PTM's are 1) very low concentrations in the open gulf, 2) higher concentrations near land, and 3) highest values in the St. Lawrence estuary. PTM concentrations increase in the salinity gradient of the estuary as the St. Lawrence River is approached. Clay minerals, quartz, feldspar, and amphibole were identified by X-ray diffraction in samples of suspended particulate matter from the estuary. The distribution of particulate iron is strikingly similar to the distribution of dissolved iron, except that the difference between estuary and open gulf is more pronounced in the former. Apparently the dispersal of PTM's by mixing is accompanied by their removal by sedimentation.

The maps of particulate Fe, Mn, and Zn give the impression that PTM's are primarily derived from the St.

Lawrence River and the other minor terrigenous inputs, but an analysis of inter-elemental variations reveals that PTM's are not homogeneously proportioned throughout the Gulf. Regional variations in PTM ratios can be visualized by making inter-element log-log plots of the PTM concentrations which has been done in Figures 6, 7. Manganese and Zn are well correlated with Fe in the estuary (stations 37 - 51), having correlation coefficients of .99 and .96 respectively. However, both correlations are nonlinear at a significance level of .995. In effect, Fe falls off faster than either Mn or Zn as the SPM is transported away from its source. Elsewhere in the Gulf, Mn and Zn deviate strongly from the regression on Fe determined by the estuarine stations. These deviations are mostly positive, i.e. enriched in Mn and Zn relative to Fe.

The high degree of correlation of Mn and Zn with Fe in the estuary indicates that all three metals are borne by the same carrier, viz, terrigenous mineral detritus. The enrichments of Mn and Zn relative to Fe in SPM outside the estuary can be explained if the SPM there contains less mineral detritus and more organic matter. The observation has been made that SPM of the estuary is 10 - 50% particulate organic matter (POM) by weight and SPM from the rest of the Gulf is 80 - 100% organic (Pocklington, pers. comm.). This generalization is based on determinations of POC and total weight of SPM on samples collected during several cruises to the Gulf of St. Lawrence.

The conclusion that Mn and Zn are enriched in the open

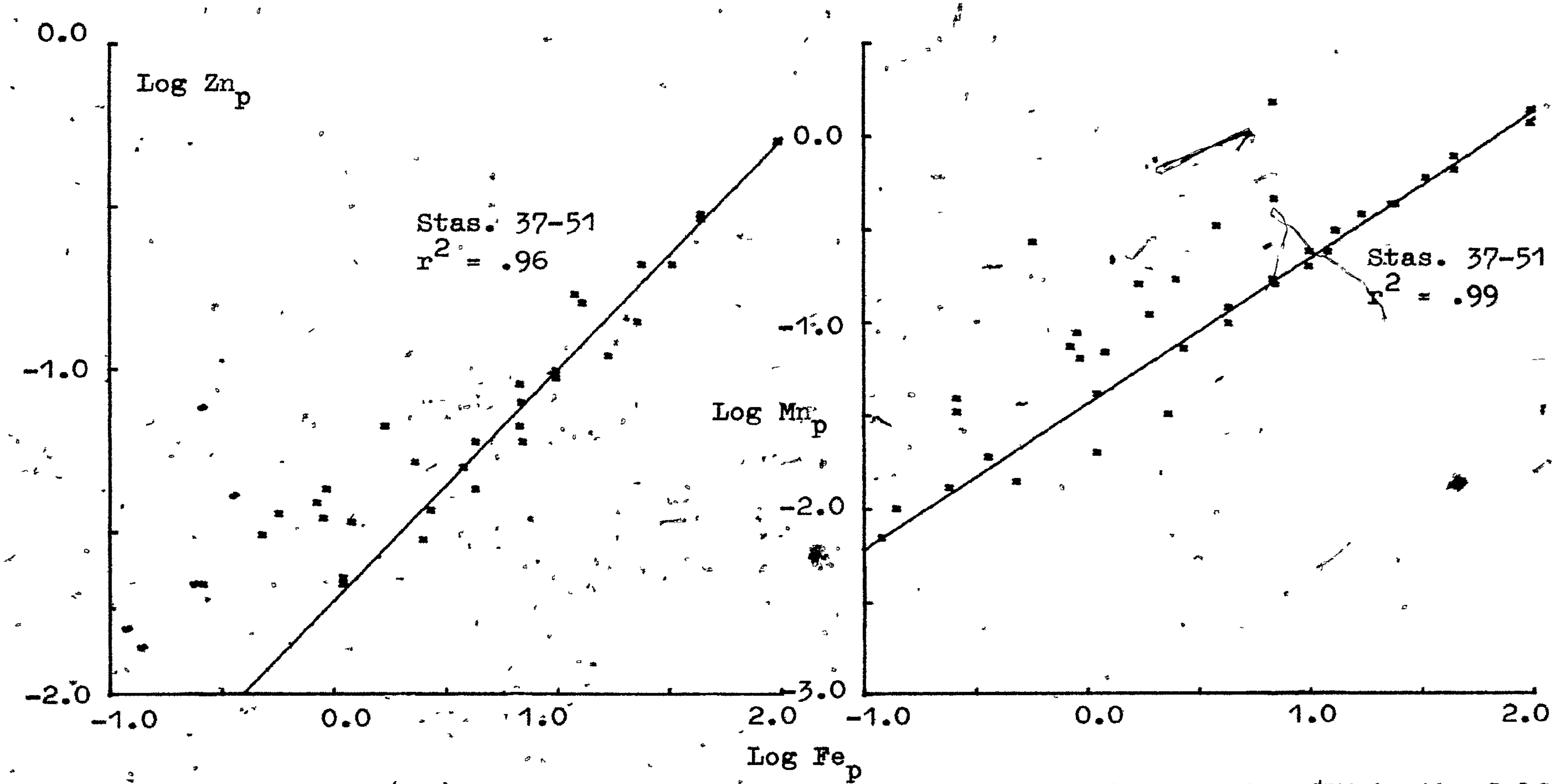

Figure 6 Log Zn_p versus Log Fe_p and Log Mn_p versus Log Fe_p diagrams for SPM in the Gulf of St. Lawrence. The regressions are based on the 15 stations of the estuary. Concentrations are ug/l.

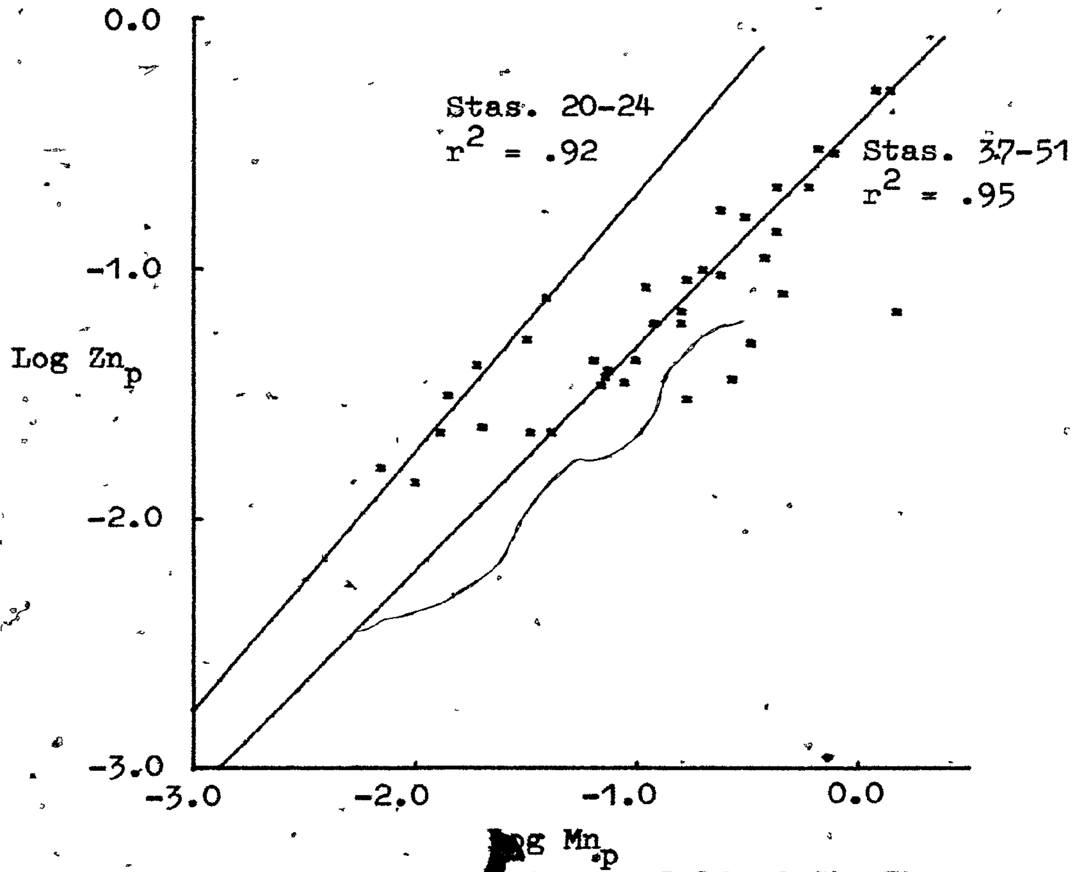

Figure 7 Log Mn_p versus Log Zn_p for SPM in the Gulf of St. Lawrence. The 5 stations of the open gulf and the 15 stations of the estuary are used to form two separate regressions. Concentrations are ug/1.

gulf by reason of their incorporation into POM can be supported by a consideration of the concentrations of Fe, Mn, and Zn in phytoplankton and suspended sediments. Since Fe has a crustal abundance of about 6%, it is used as a reference element for suspended sediments (Taylor, 1964). Zinc has an enrichment factor of 3.0 in SPM of the estuary and one of 70. - 200. in the open gulf. Similarly, the enrichment of Mn is -0.3 in the estuary while the enrichment for the open gulf is 2.0 - 8.0. Comparing these with enrichment factors for phytoplankton computed using the data of Martin and Knauer (1973), it can be concluded that the enrichment of Zn in phytoplankton is very similar to that for SPM in the open gulf, and Mn appears to be more enriched in SPM of the open gulf than in phytoplankton. Manganese data in the Gulf are concordant with particulate Mn measured during the bloom of phytoplankton in St. Margaret's Bay, however.

The highest enrichment of Zn occurs in the open gulf, but this is not true for Mn. The plot of log Zn vs log Mn in Figure 7 shows that Mn and Zn are well correlated in the estuary as expected. The fact that a good linear fit is also obtained for the stations of the open gulf suggests that another carrier is involved in that region. The two parallel regressions account for most but not all of the variability of Mn and Zn. These facts lend further support to the interpretation that two different carriers, organic and mineral, control the disposition of PTM's in the Gulf. The organic carrier, being both phytoplankton and detrital

POC, may have a variable composition. This fact might explain some of the residual variability which does not seem to be accommodated in such a simple model.

Several other studies (Spencer and Sachs, 1970; Abdulla and Royle, 1974; Wallace et al, 1976) have found PTM distributions to be controlled by mineral and organic carrier phases. Perhaps the most relevant is the study of PTM's in the Bristol Channel. Abdulla and Royle observed that Zn, Mn, Cu, and Cd exhibited unusually high concentrations in SPM of the outer channel in June when compared with their levels in April. They attributed the elevation of these metals to their concentration by phytoplankton. This interpretation was sustained by nutrient studies of the region and by the demonstration of a linear relationship between the metals and particulate nitrogen in the outer part of the channel. The conclusion, gleaned from PTM correlations in the Gulf of St. Lawrence, that aluminosilicate minerals become less important carriers of particulate trace metals away from estuaries and toward the open sea is also supported by other findings. Wallace et al (1976) measured trace metals and particulate organic carbon in a series of surface bucket samples between the New England coast and Bermuda. Examining PTM variations with respect to Al_p and POC, they concluded that organic matter is the probable regulator of PTM's in surface waters of the open oceans, and aluminosilicate minerals, though probably present, are carriers of minor importance for most trace metals.

Thus the tendency displayed by Mn and Zn to be enriched relative to Fe in the open gulf can be explained by the increasing proportion of particulate organic matter relative to particulate mineral matter. It does not necessarily follow that biological means are the only way that trace metals are removed from waters of the gulf. The non-linear relationships noted between Fe and either Mn or Zn in the estuary could be caused by gradual adsorption or precipitation of all three metals onto lithogenous particles in roughly equal proportions. The amounts of Fe, Mn, and Zn incorporated into a hydrogenous phase would be only a few per cent of ambient dissolved concentrations. It is also possible that the observed effects are due to fractional settling of the larger (Fe rich) particles as the suspended load traverses the length of the estuary (which takes about 15 days).

In summary, the distribution of particulate Fe, Mn, and Zn in surface waters of the Gulf of St. Lawrence is controlled by the input of terrigenous detrital material from the St. Lawrence and other rivers and by nonconservative processes in situ. In the open water portions of the gulf, it appears that Zn, Mn, and possibly Fe are predomintly derived from phytoplankton and detrital organic matter, whereas in the estuary all three metals owe their origin to riverborne detrital minerals. The significant covariation of dissolved Zn, Cu, and Mn in the estuary with salinity and nitrate suggests that these metals are controlled by biological processes. The existence of a potent sink for Fe and Mn in the open gulf indicates that these metals are removed from surface waters of the open gulf on a time scale comparable with the circulation of water. One cannot tell from the evidence whether biological production or adsorption-precipitation is the more important means of removing trace metals from surface waters of the gulf.

III Trace Metal Observations in St. Margaret's Bay

There have been several attempts to study the accumulation of trace metals by plankton in the marine environment, but a clear understanding has not yet evolved. Morris (1971) observed variations in Mn, Cu, and Zn during an intense bloom of Phaeocystis which indicated that the metals were perturbed by the bloom, but apparently in quite different ways. All three metals were concentrated by the organism, but at different times. In the seawater, Mn decreased, Zn increased, and Cu stayed about the same coincident with the bloom. Morris tentatively proposed that the metals were incorporated into the bodies of the organism in different ways. Knauer and Martin (1973), after a one year study of Cd, Cu, Mn, Pb, and Zn in the surface water and phytoplankton of Monterey Bay, concluded that with the possible exception of Cd during peak productivity, metal levels in nearshore waters appeared to be more dependent on hydrographical fluctuations than on biological factors.

From the elemental composition of phytoplankton (Martin and Knauer, 1973; Riley and Roth, 1971), it would appear that an observable depletion of some trace metals might take place during the spring flowering in nearshore temperate seas. To test this hypothesis, a weekly sampling program was begun in St. Margaret's Bay where dissolved and particulate trace metals were followed from March 2 to May 9, 1976. The chosen sampling location, station M, is approximately in the center of the bay where the water is

29 fathoms deep. In order to minimize the chances of contamination, a special sampler (Top-drop Niskin) was employed which did not contain an internal spring or shock cord. Within 24 hours of collection, samples were filtered and acidified as described in "Trace Metal Patterns in the Gulf of St. Lawrence". The analysis followed the procedures described in the Appendix.

St. Margaret's Bay is a small embayment, about 8 x 16 km, with a slight sill at its broad entrance. The bottom topography is relatively uniform, and depths range up to 80 metres near the mouth on the western side. The ratio of the fresh water inflow to tidal inflow is small, so that any vertical two layered circulation is small. The residence time of water in the bay is about 10 days in the upper layer and 30 days in the lower layer; the mean flushing results principally from the anticlockwise circulation of shelf water through the bay (Heath, 1973).

In general, water properties in St. Margaret's Bay result from the interplay between local conditions (insolation, precipitation, winds, etc.) and oceanic water. Temperature and salinity measurements made during March and April at station M reflect the changing seasons. During winter, stratification is maintained by salinity differences, and temperature increases slightly from top to bottom. By March 9, the thermocline is developing and heavy spring rains show up as low salinity events in the surface layer.

From this point on, the water column behaves as two layers, a mixed layer of warm low salinity water about 10 metres thick overlaying more saline water of oceanic origin.

The annual cycle of primary productivity in St. Margaret's Bay follows the usual pattern for temperate coastal waters, with a major peak in spring and a minor one in autumn. The spring bloom usually peaks in mid-April when a maximum rate of 2000 ± 700 mg C/m^2day may be attained (Platt, 1971). Except during the spring flowering, nutrient levels in St. Margaret's Bay are probably controlled more by water movements on the continental shelf than by biological processes within; weather disturbances in late summer and autumn can cause complete water replacement in relatively short periods of time (Platt et al, 1972). The growth of phytoplankton was monitored by Secchi depth and chlorophyll a measurements. Biological production was monitored by observing the depletion of nitrate in the water column. According to these indicators, the bloom of April 1976 was similar in most respects to the one studied by Platt and Subba Rao (1970) in 1969.

Before delving into the results of the temporal study of dissolved Fe, Mn, Cu, and Zn, it is perhaps useful to anticipate the kinds of variability that might be encountered. Since the trace metal data are three dimensional, two kinds of variability, those of sampling date and sample depth can be analyzed. The causes of these may be either physical, biological, or chemical. Fresh water is expected to be the main contributor to variations in dissolved trace metal concentrations in the bay. The effects of fresh water will be largely confined to the surface layer. Longer period variations in the deep water may occur as a result of advection, diffusion from the sediments, and biological uptake. If biological uptake of dissolved trace metals is to occur during the bloom, day-to-day changes in dissolved trace metals should parallel those of nitrate. Other possible causes of nonconservative behaviour, such as adsorption and precipitation, are expected to be minor in this salinity regime, compared to biological ones.

The Changes in Dissolved Trace Metals

The concentrations of Fe, Mn, Cu and Zn display definite trends with depth in the water column. Figure 8 depicts some typical profiles of the four metals. It is evident that the dissolved metals are generally higher in the surface layer than in the deep layer, and that sharp gradients exist in the upper 10 metres. Below about 10 metres the water is more nearly uniform, but Fe and Mn are usually higher at 40 metres than at 25 metres. The nature of these profiles can be better understood if metal concentrations are plotted against salinity as in Figure 9. The relationship of Fe and Mn to salinity is decidedly non-linear. If only conservative mixing of two waters of differing salinities and trace metal concentrations controlled the abundance of Fe and Mn in the water column, the intermediate points would all lie on a straight line connecting the two end members. Departure from a linear relationship with salinity

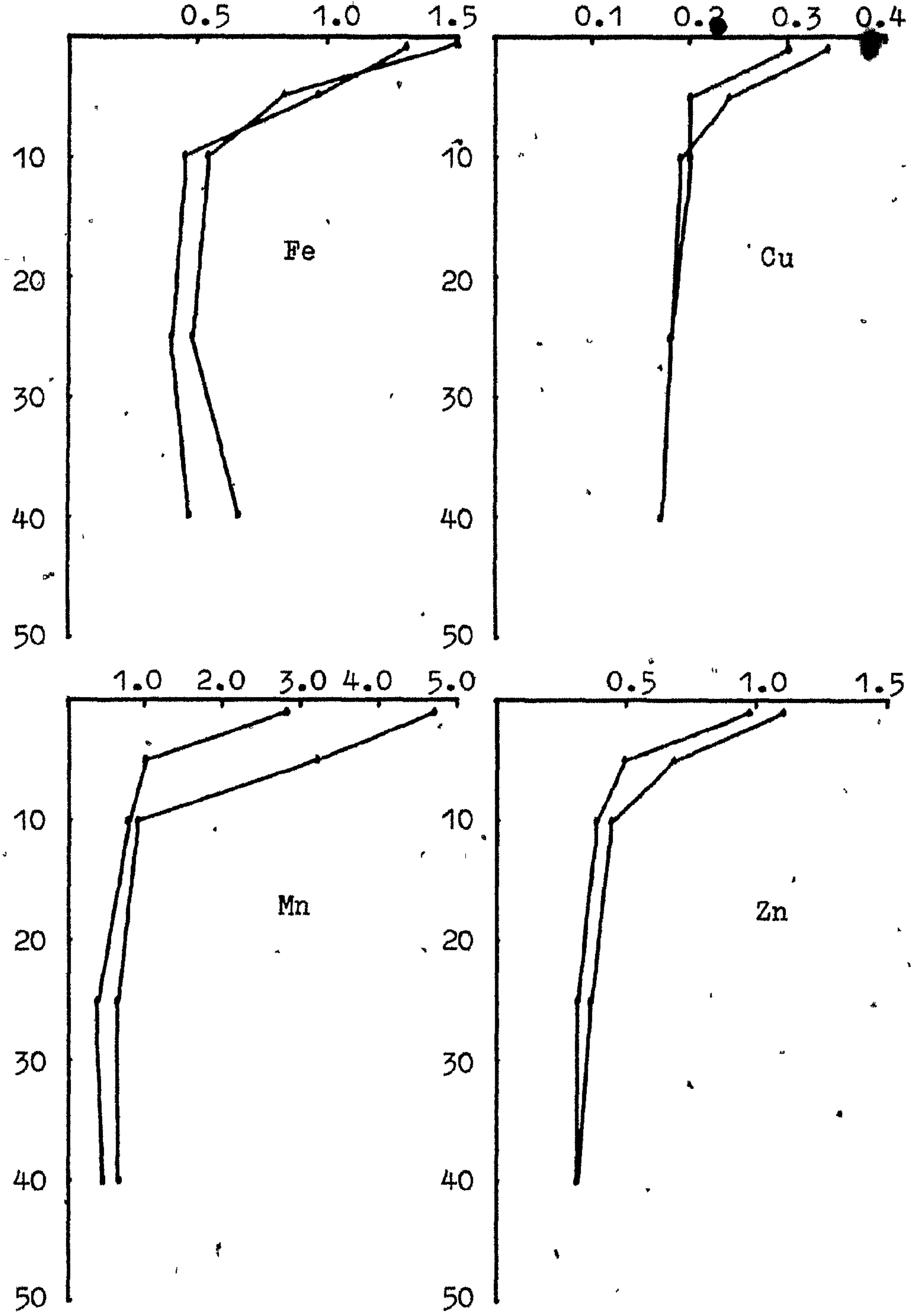

Figure 8 Some typical profiles of dissolved Fe, Mn, Cu, and Zn at station M, St. Margaret's Bay. The data consists of the sampling days, March 16 and 23. Concentrations are µg/l and depths are metres.

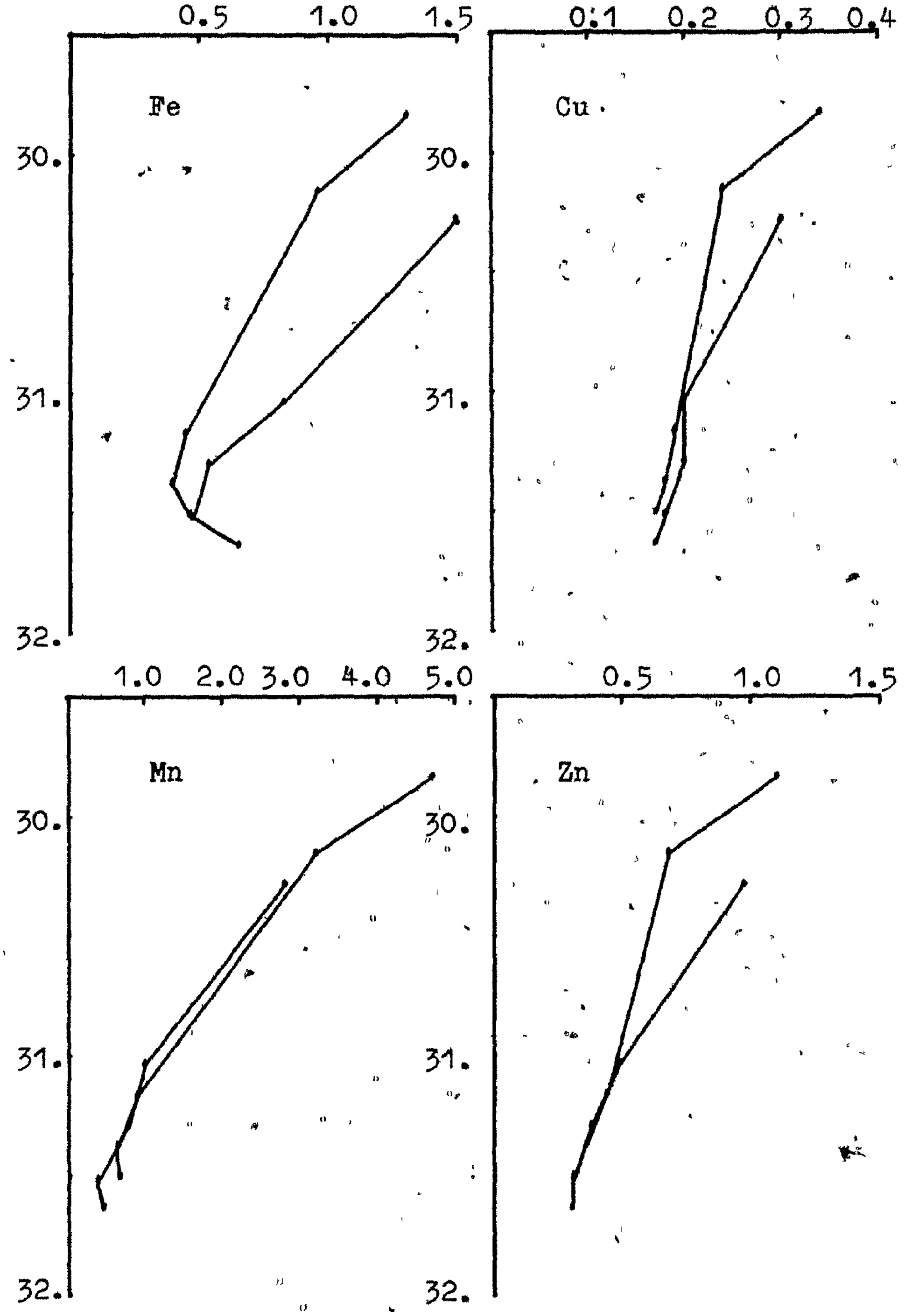

Figure 9 Dissolved metal versus salinity diagrams for the profiles of Figure 8. Concentrations are µg/l and salinities are ppt.

implies that there are more than two water types or that nonconservative processes are involved. Since this curvature is not a transient feature, it is likely that there is a source at the bottom or a sink at mid-depths. Nonlinearity in the profiles of Cu and Zn cannot be demonstrated.

Day-to-day variations in trace metal content of St. Margaret's Bay are depicted in Figures 10 - 13. It is evident that concentrations do vary with time and that appreciable changes can occur over short periods. The order in which the elements are perturbed by fresh water is Mn > Fe > Zn > Cu. Two incursions of fresh water occured on March 16 and March 23. These events are easily spotted in the records of Fe, Mn and salinity (Figure 14). In general there is an overall correspondence of salinity fluctuations in the surface layer with rainfall (Figure 15). Iron and Mn fluctuations are generally well correlated with those of salinity in the surface layer but not at depth. It is possible to show by correlating Mn concentrations between adjacent depths that the water column has a two-layered structure, i.e. that fluctuations in the deeper water are in effect decoupled from those occurring in the surface layer (0-10 m). Thus, day-to-day variations caused by fresh water input are appreciable but confined to the surface layer. The deep water is more oceanic and apparently more time-stable. These observations are in accord with the physical features of St. Margaret's Bay mentioned earlier.

During the period of the bloom, April 2 - April 26, dissolved Fe and Mn exhibited a decrease throughout the

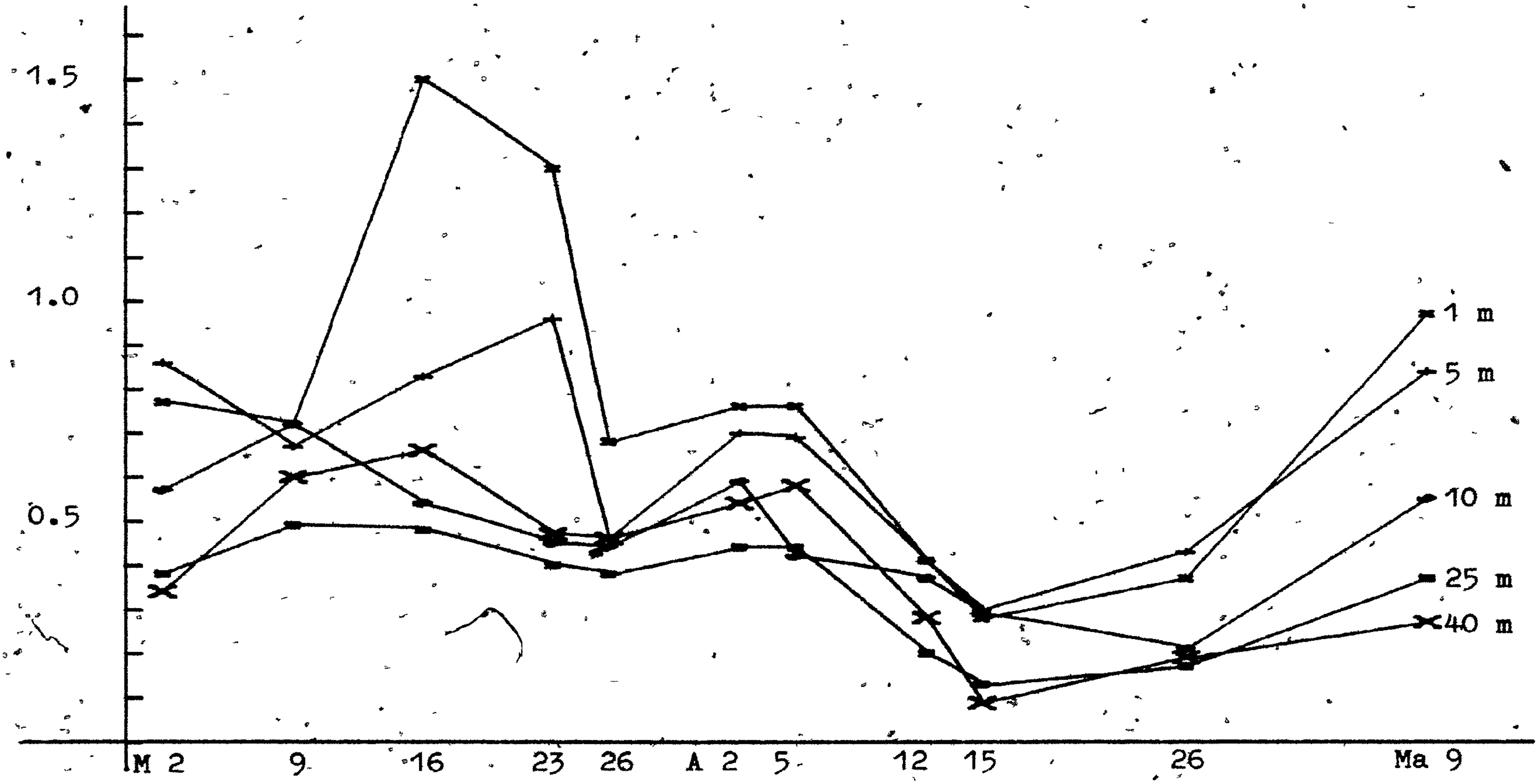

Figure 10 Dissolved Fe at 1,5,10,25,40 meters versus sampling day at station M, St. Margaret's Bay. Concentrations are µg/l.

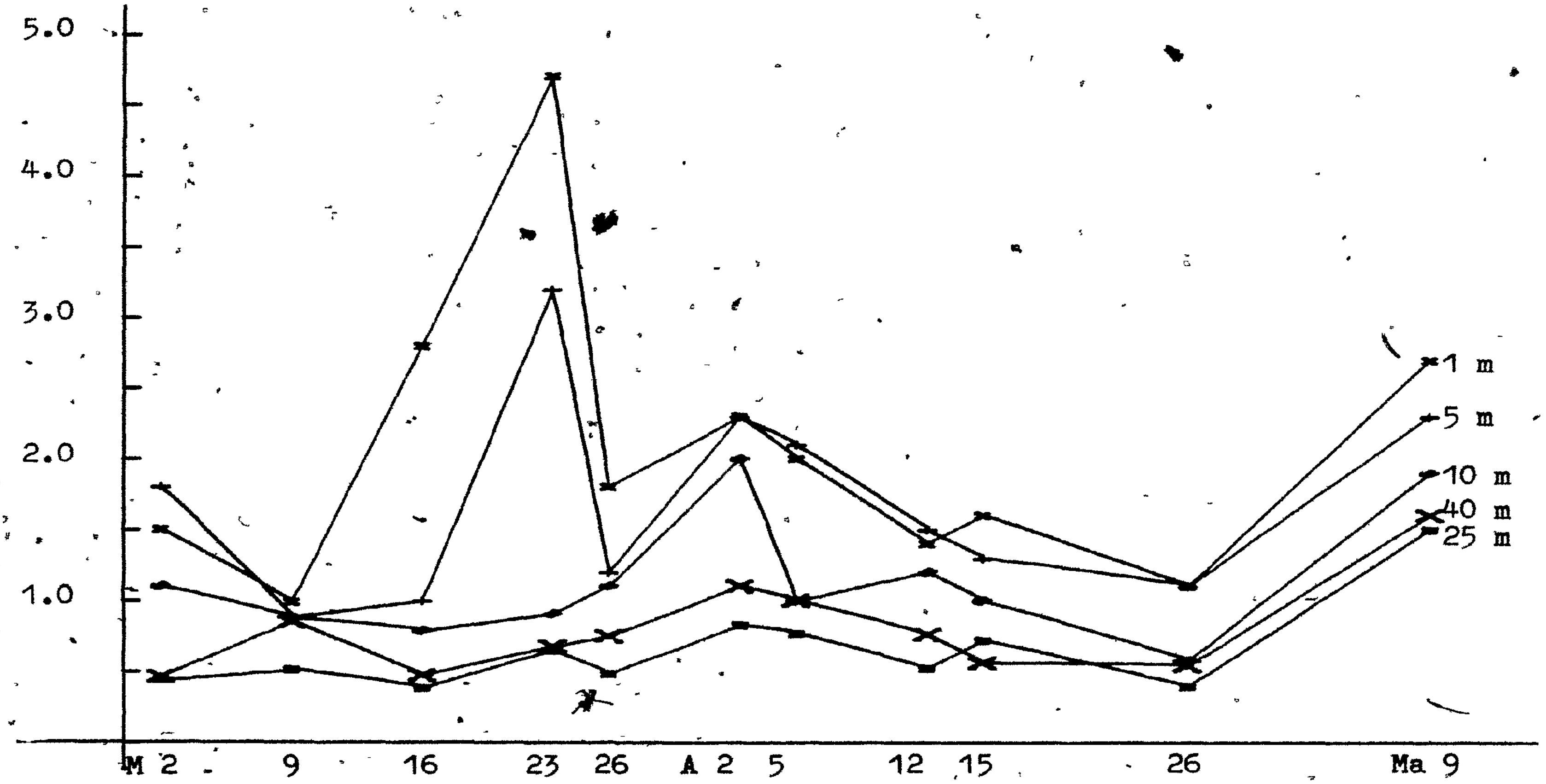

Figure 11 Dissolved Mn at 1,5,10,25,40 meters versus sampling day at station M, St. Margaret's Bay. Concentrations are μg/l.

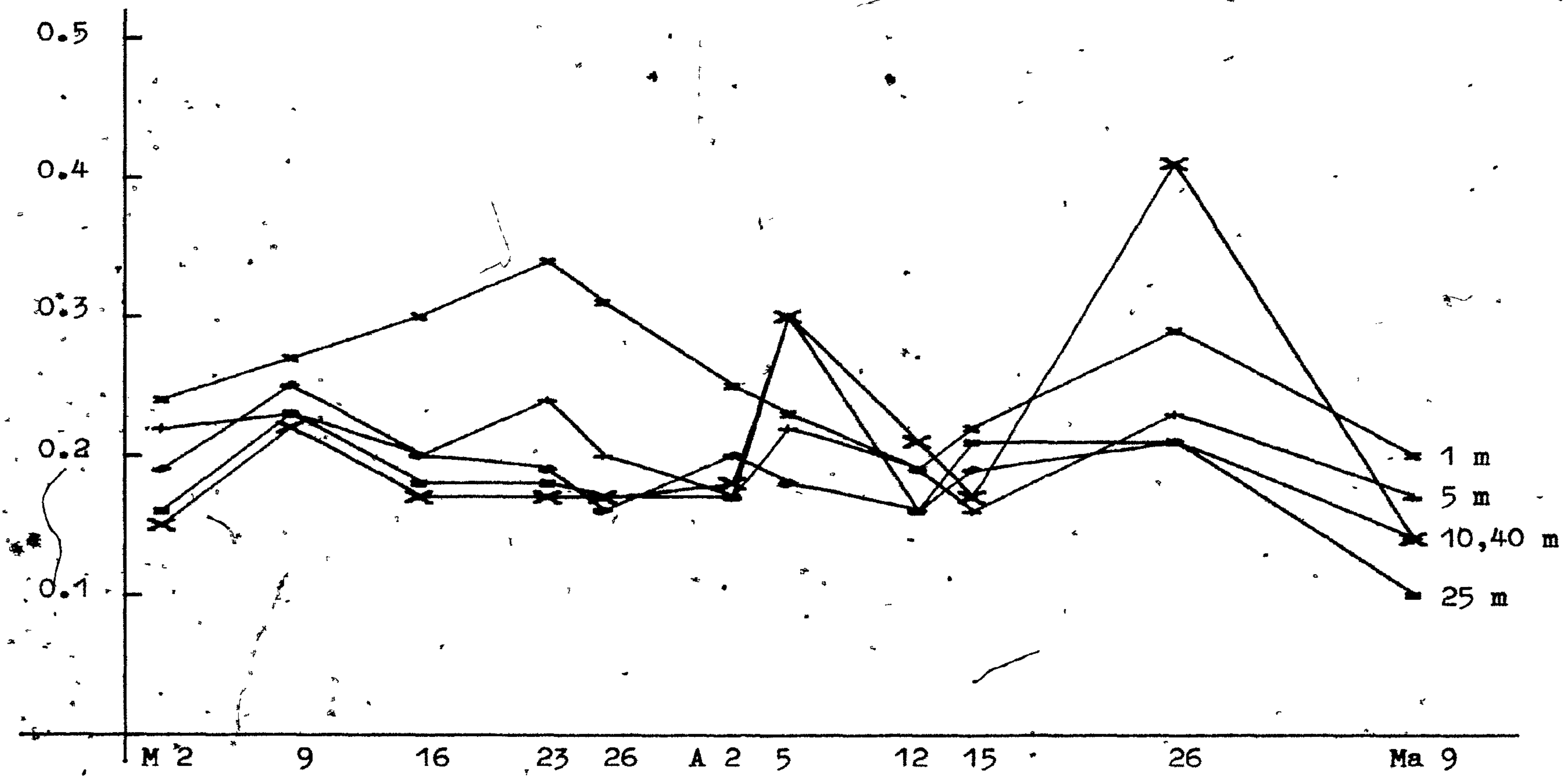

Figure 12 Dissolved Cu at 1,5,10,25,40 meters versus sampling day at station M, St. Margaret's Bay. Concentrations are µg/l.

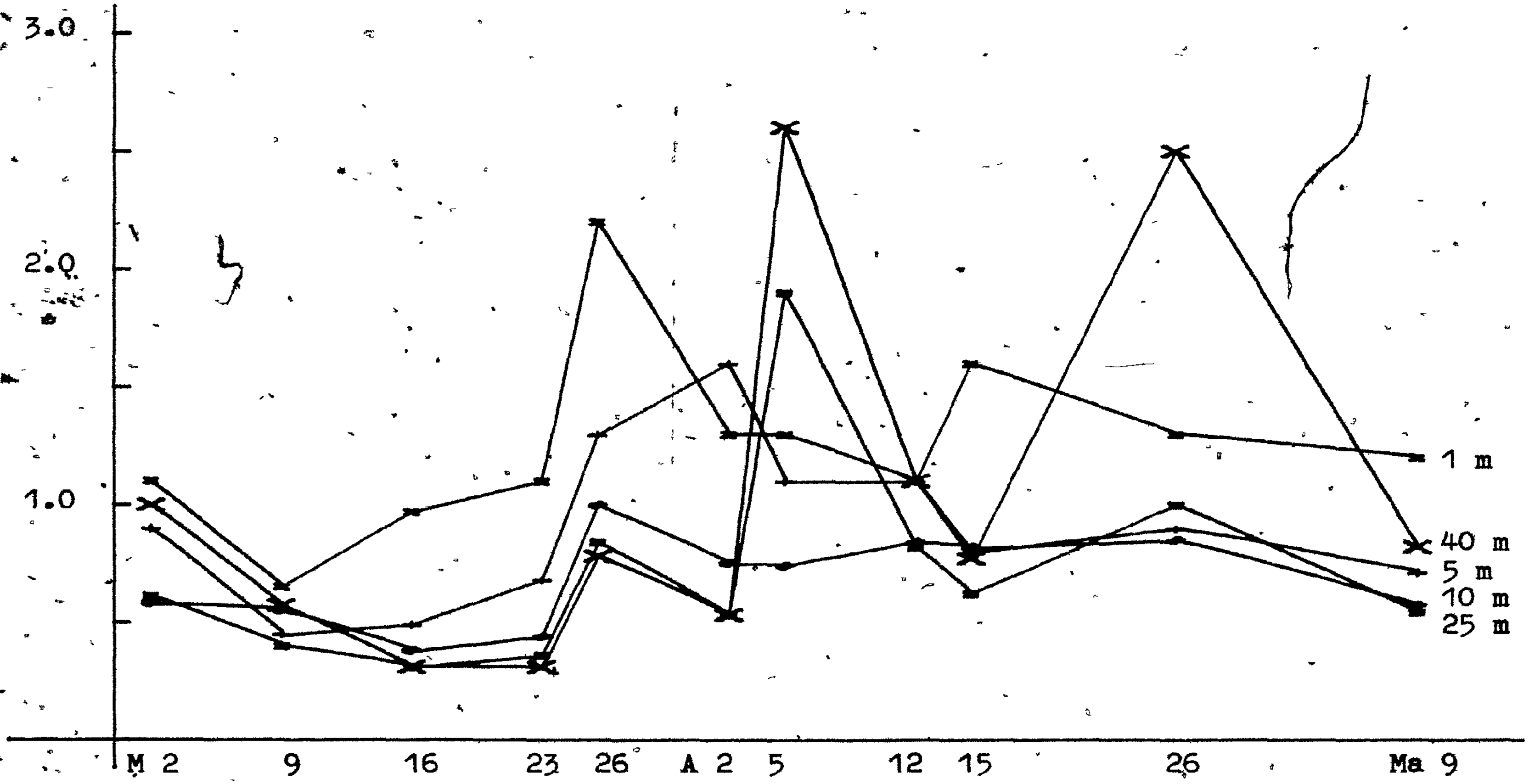

Figure 13 Dissolved Zn at 1,5,10,25,40 meters versus sampling day at station M, St. Margaret's Bay. Concentrations are µg/l.

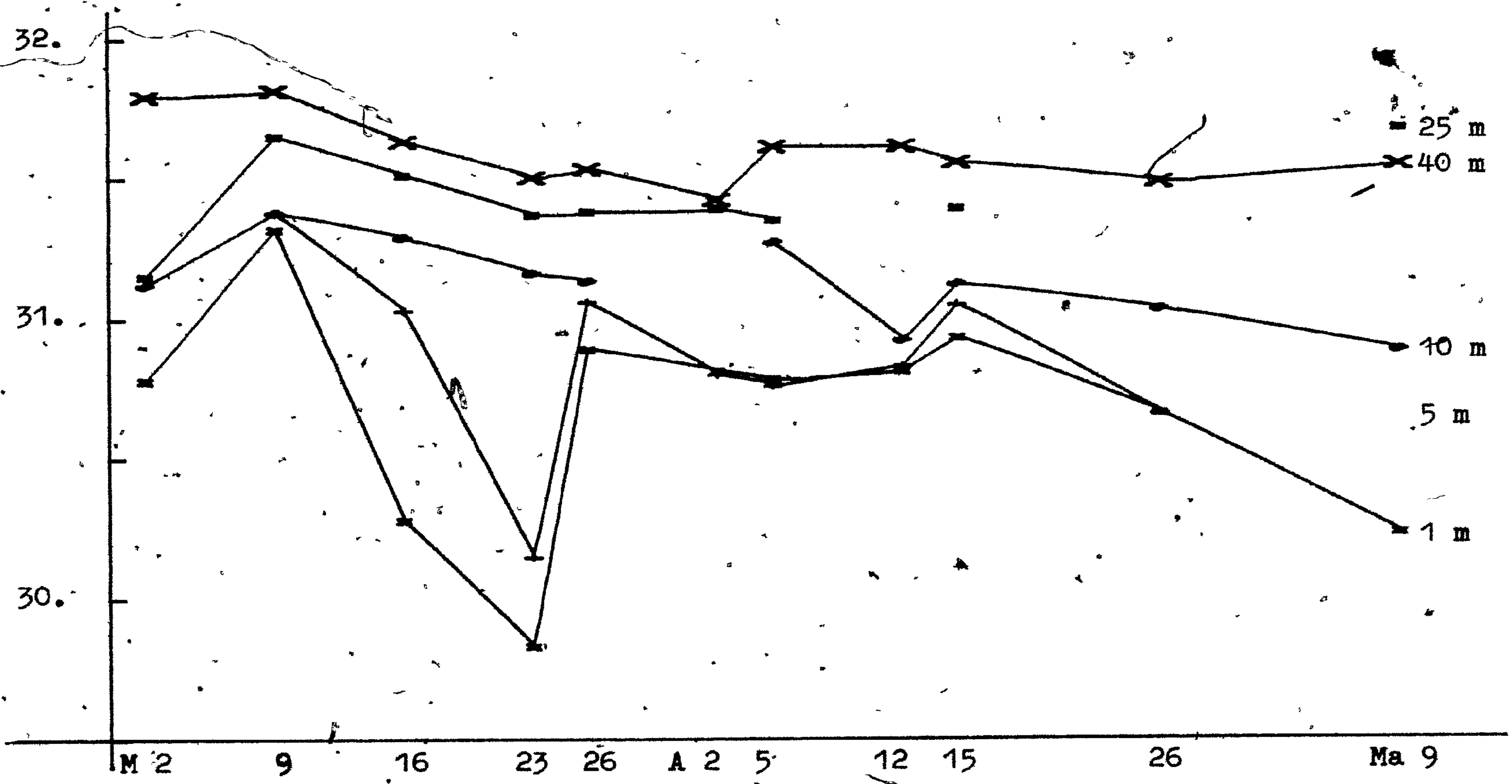

Figure 14 Salinity at 1,5,10,25,40 meters versus sampling day at station M, St. Margaret's Bay. Salinities are ppt.

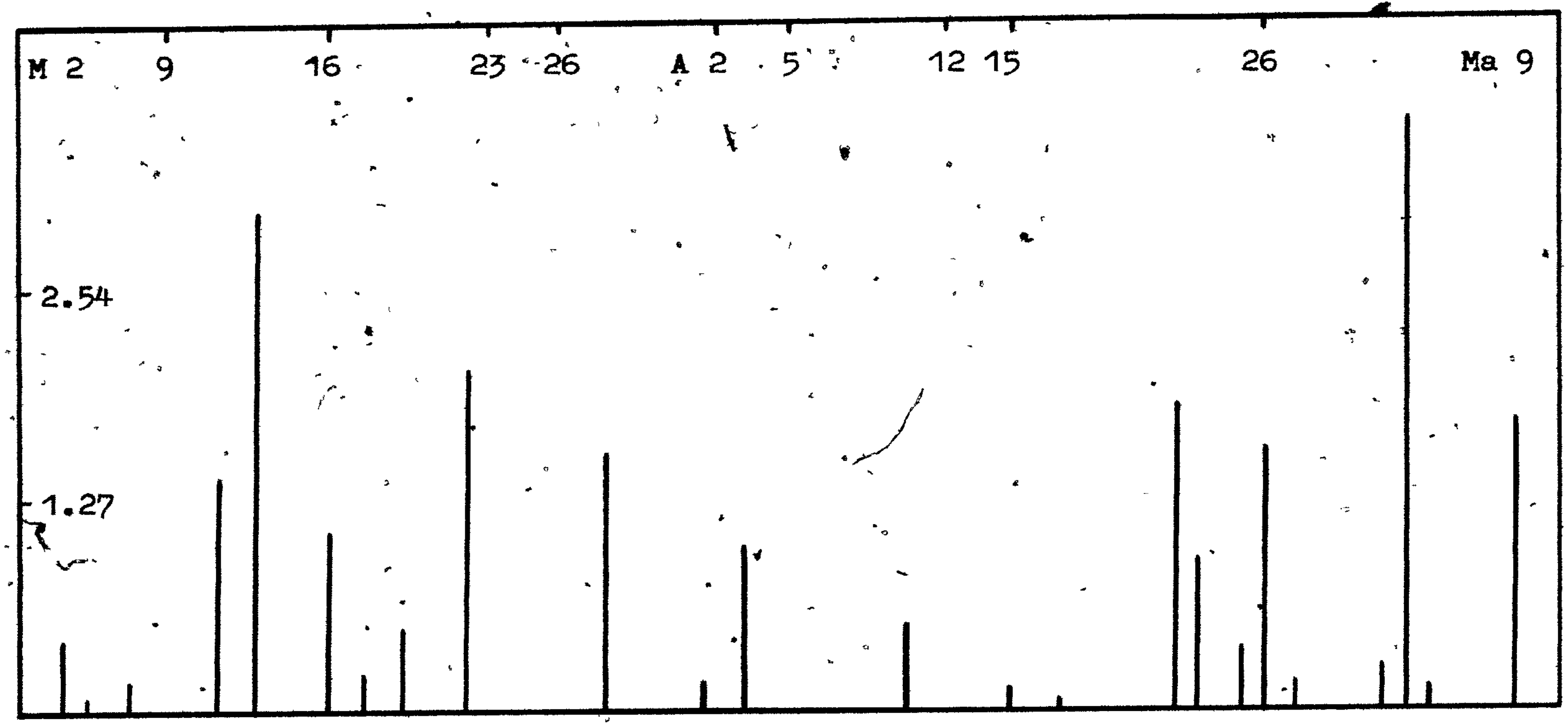

Figure 15 Average precipitation for St. Margaret's Bay during the study interval. Precipitation is centimeters.

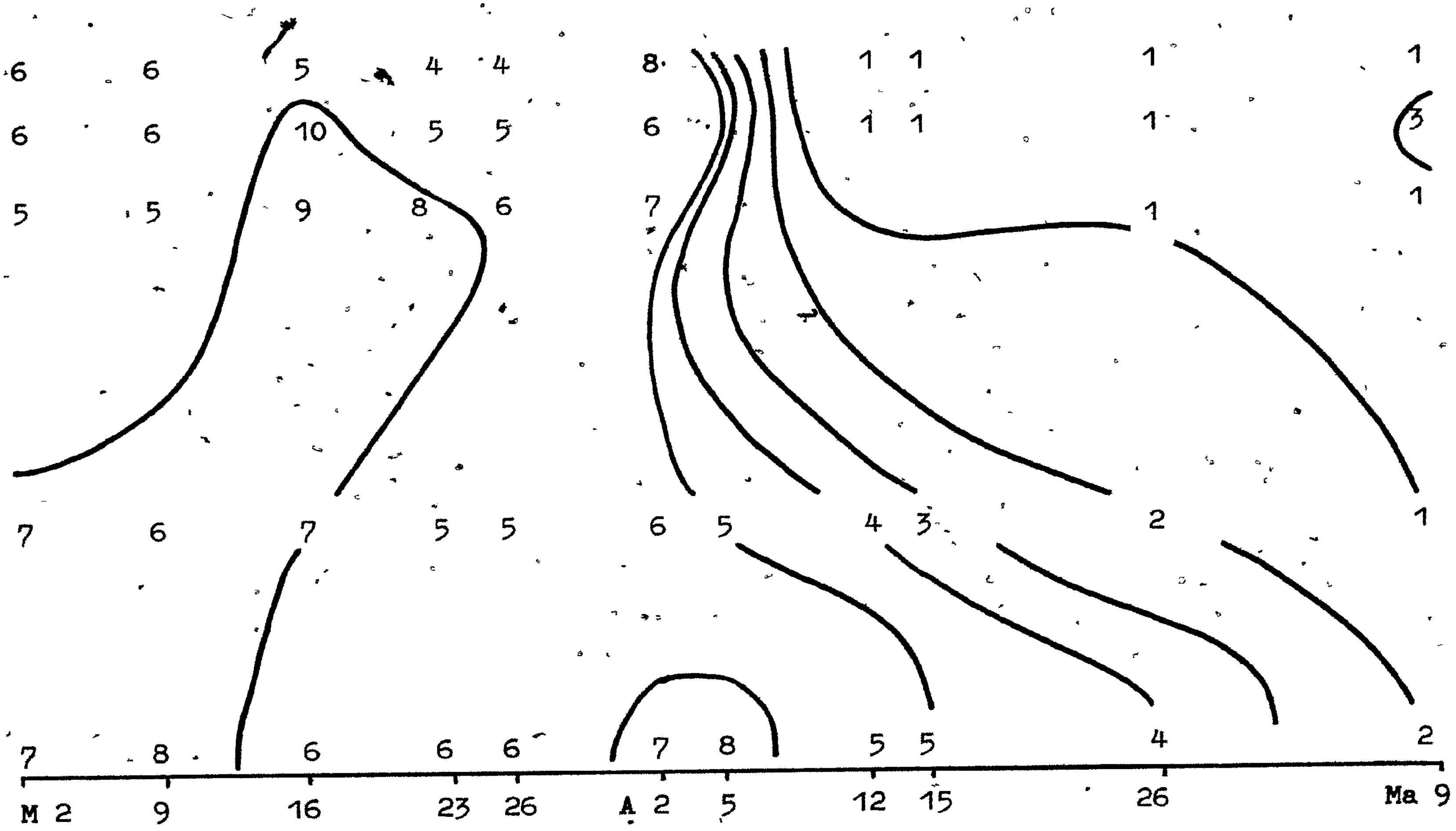

Figure 16 Contour map of Nitrate at station M, St. Margaret's Bay during the study interval. Concentrations are µg-at/l.

entire water column which was precipitous in the case of Fe and gradual in the case of Mn. The decline of nitrate began on April 2 and continued through May 9 (Figure 16). Also during this period, precipitation lulled somewhat and surface salinities remained constant. By May 9 rainfall had resumed, and salinities accordingly, dropped slightly. Iron and Mn returned to higher values at all depths on May 9, but nitrate remained very low. The decline of Fe and Mn during the bloom may have occurred naturally by the growth of phytoplankton. Indeed this was expected for Fe, since it is often present in very high concentrations in phytoplankton (Martin and Knauer, 1973). In order to test this hypothesis, Fe, Mn, and NO_3 concentrations were integrated in the water column $(\sum c_i(z_{i+1} - z_i))$ and regressions were formed between the metals and nitrate during the relevant period (April 2 - April 26). These regressions are displayed in Figure 17; it can be seen that there is indeed a good correlation in both cases. In the case of Fe, only one of the eleven sampling days, May 9, falls outside of the relationship. The regression of Fe on NO_3 is very significant; the probability that it is due to chance is .025. Manganese correlates with NO_3 only during the five days when NO_3 is rapidly depleted (April 2 - 26). The significance level of this regression is 90%. It is clear that the parallel behaviour of Fe and NO_3 before and during the spring bloom implies the removal of dissolved Fe by phytoplankton production. Manganese is probably also removed, but to a lesser extent compared with its normal concentrations in the water.

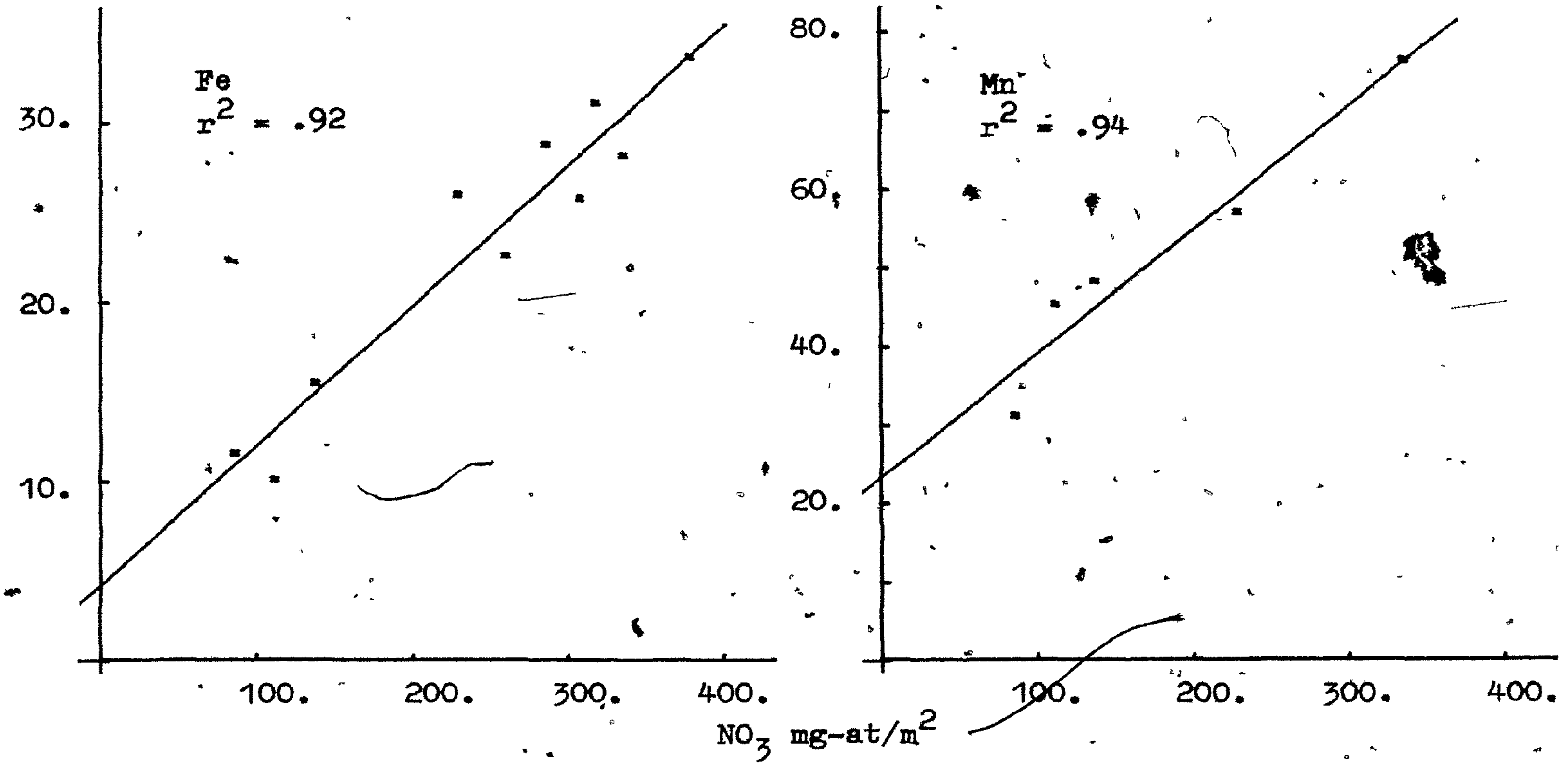

Figure 17 Regressions of integrated Fe_d and integrated Mn_d against integrated NO_3. The regression of Fe vs NO_3 is based on 10 sampling days from March 2 through April 26, while the regression of Mn vs NO_3 includes 5 sampling days, April 2 - 26. Iron and Manganese concentrations are mg/m^2.

From the slopes of the regressions of Fe and Mn with nitrate, it is possible to estimate the utilization ratios. The atom ratios for Fe and Mn turn out to be 1.39×10^{-3} and 2.86×10^{-3} respectively. Since the net removal of nitrate from the water column between April 2 and April 26 is 250 µg-at/m^2, the net removals of Fe and Mn by biological production are calculated to be .39 µg/l and .78 µg/l respectively. These are obviously substantial proportions of the normal steady state concentrations of the elements in the bay. Estimates of the phytoplankton utilization of dissolved Fe and Mn will be compared with concurrent changes in the concentrations of particulate Fe and Mn in the discussion of particulate trace metals to follow.

Considering for a moment the temporal behaviour of Cu and Zn depicted in Figures 12 and 13, a more random picture is presented. There is evidence that some of the samples were contaminated, e.g. in the singularly high concentrations at 25 and 40 metres on April 5 and April 26. Because there is little correspondence of the day-to-day variations of Cu and Zn with any known factors, it is felt that much of the variability can be attributed to contamination. The source of contamination is not known, but it may have been the sampling device itself. A possible source of Zn is the neoprene gasket material used in the fabrication of the "Top Drop Niskin" sampler. Because contamination is suspected, a complete interpretation of the behaviour of dissolved Zn and Cu is not attempted.

The Changes in Particulate Trace Metals

Typical of nearshore coastal waters, the average weight of SPM in St. Margaret's Bay is about 1 mg/l. This is higher than is characteristic of the Scotian Shelf, but much lower than some shallow estuarine environments, e.g. Narragansett Bay. Measured surface concentrations of particulate-Fe in St. Margaret's Bay are comparable with the values noted for nearshore stations in the Gulf of St. Lawrence (Figure 2). The fraction of SPM that is organic can be estimated by subtracting the weight of aluminosilicate minerals ($\doteq 10 \times Al_p$) from the total weight of SPM. What is actually calculated is the non-aluminosilicate fraction which is certainly an over-estimate of POM, but the result suggests that a substantial proportion of the SPM in St. Margaret's Bay is organic. This is supported by the POC determinations of Platt and Irwin (1968) and of Sutcliffe (1972). Although total SPM does not generally show a trend with depth, the per cent of SPM that is aluminosilicate increases with depth. The aluminosilicate fraction at 25 and 40 metres, averaged over the entire sampling period, is 15%, while the average value for 1, 5, and 10 metres is 8%. The difference between surface and deep water is greater than the depth-averaged daily variations. There is only a slight tendency for the per cent aluminosilicate to decline after March 26 during progress of the plankton bloom. These facts are consistent with the interpretation that there is a high background of detrital organic and inorganic SPM in the bay which tends to obscure the effect of a bloom of phytoplankton on total suspended particulate matter.

A salient feature of PTM concentrations in the water column is that they increase with depth. The exponential-like increase is depicted by the average profiles of Fe and Al in Figure 18. These profiles suggest that Fe and Al owe their existence in the water column primarily to the resuspension of bottom sediments. The average profiles of Mn, Zn, and Cd shown in the same figure do not closely follow those of Fe and Al, suggesting that these metals are not entirely carried by resuspended aluminosilicate material. There is a considerable amount of daily variation in the level of aluminosilicate minerals. The highest levels occurred on March 23 following an intense storm (March 17); the lowest level was measured on May 9. As with SPM, particulate Al decreased in the latter days of the study interval owing to thermal stratification and reduced resuspension.

High background levels of SPM tend to mask the effects of the spring bloom on PTM levels, but when Mn, Zn, and Cd are referred to Al, the ratios manifest changes which are directly caused by in situ biological activity. When PTM/Al ratios are plotted against time, it is evident that Zn, Mn, and Cd become more concentrated relative to Al as the sampling period progresses. The five sampling days of March are considered to be pre-bloom; the Secchi depth was 8 metres and chlorophyll a was relatively low and constant. PTM/Al ratios also remained relatively low and constant during March and homogeneous with depth. Between March 26 and April 2, PTM/Al ratios begin to undergo a transition which

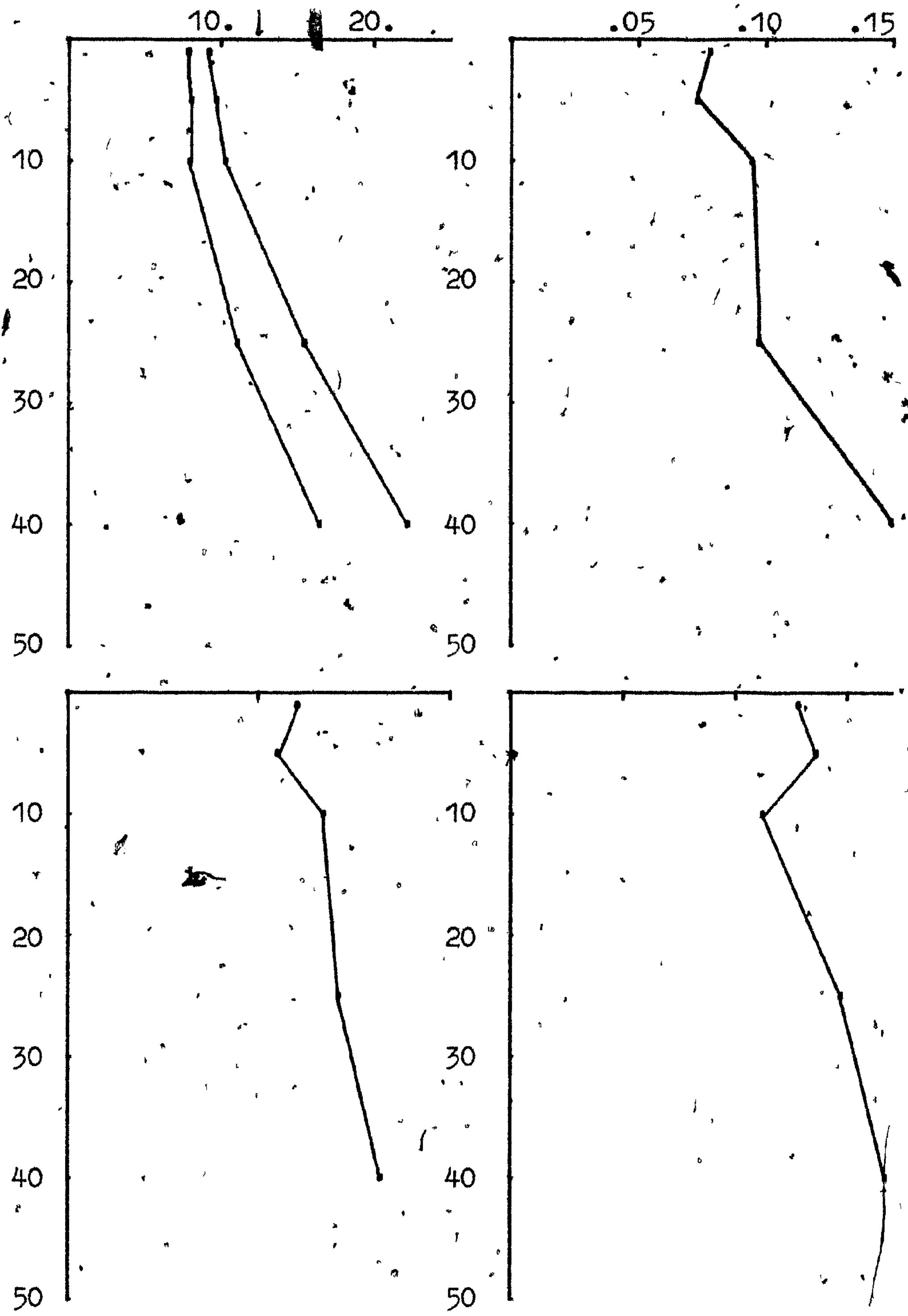

Figure 18 Particulate trace metal profiles at station M, St. Margaret's Bay, averaged over the sampling interval, March 2 - May 9. Concentrations are µg/l and depths are metres.

coincides with the onset of the bloom; the transition is toward increasing ratios. Also, the water column becomes vertically differentiated as Fe, Mn, Zn, and Cd become more concentrated in the surface. The increases in these metals relative to Al are partly due to biological fixation of these metals in phytoplankton and partly to a gradual decline of resuspended aluminosilicates subsequent to stratification of the water column. The PTM/Al ratios observed before and during the bloom in St. Margaret's Bay can in general be rationalized by comparing these with ratios calculated from data on phytoplankton and clays, as was done for PTM's in the Gulf of St. Lawrence.

If the simplifying assumption is made that PTM's are borne by two carriers, aluminosilicate and organic, it is possible to estimate the magnitude of the organic fraction by subtracting from the total PTM the contribution of the aluminosilicate fraction, i.e. $PTM_{organic} = PTM_{total} - (PTM/Al)_{Al-Si} \times Al_p$. Since PTM/Al ratios for the mineral fraction of resuspended sediments were measured only indirectly, the values of $(PTM/Al)_{Al-Si}$ were constrained to minimize non-detrital PTM concentrations. This arbitrary normalization of the non-detrital or organic fraction enables the effect of the phytoplankton bloom to be seen in Figure 19. It is apparent that there is a marked difference between March and April in the tendency of Mn and Zn to be associated with the organic carrier. Cadmium also manifests a transition from aluminosilicate carrier to phytoplankton, but for Fe the change is less noticeable.

Figure 19 depicts the temporal changes in depth-averaged particulate Fe, Mn, Zn, and Cd at station M, St. Margaret's Bay. The upper curve is that of total PTM, while the lower curve is that of non-aluminosilicate PTM. The averaging function is, $\sum c_i(z_{i+1} - z_i)/50$. The assumed PTM/Al ratios for aluminosilicate material are the following: Fe/Al = .643, Mn/Al = .0285, Zn/Al = .00399, and Cd/Al = .0000750. Concentrations are µg/l.

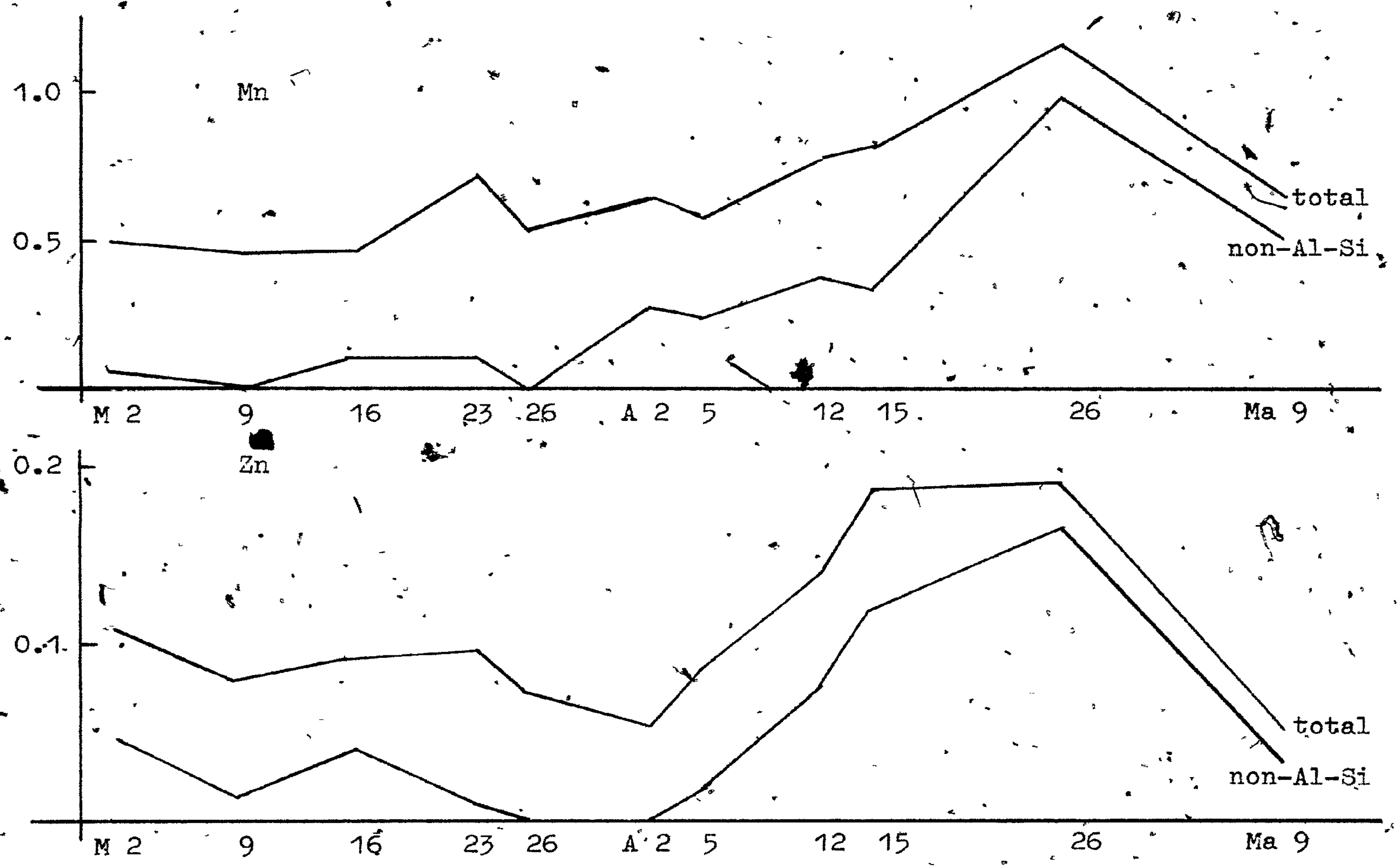
Mn
1.0
0.5
total
non-Al-Si
M 2
9
16
23
26
A 2
5
12
15
26
Ma 9
Zn
0.2
0.1
total
non-Al-Si
M 2
9
16
23
26
A 2
5
12
15
26
Ma 9

Figure 19

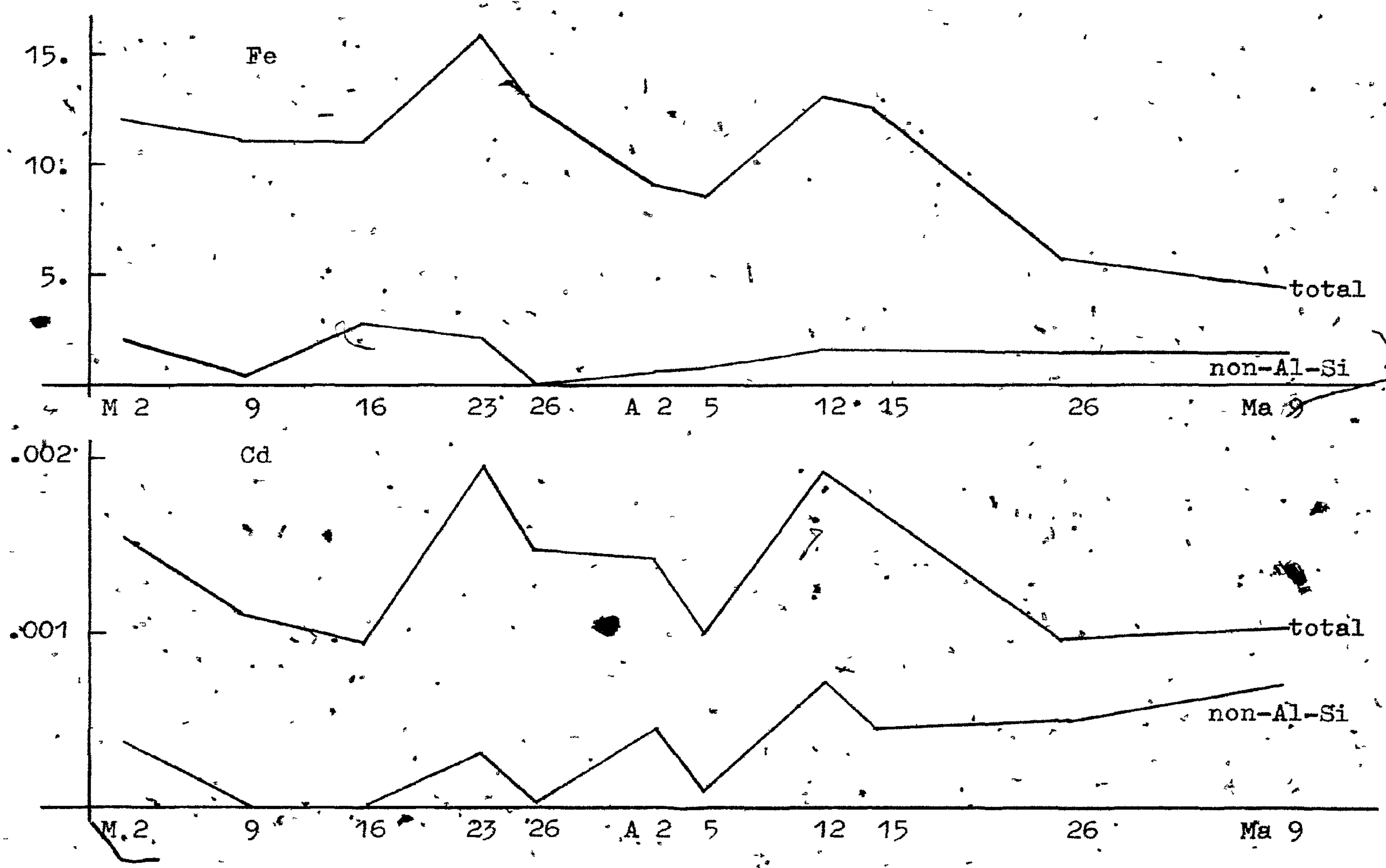

Figure 19, continued

That is because Fe is a major element in the crust and is thus present largely as mineral particles. Also since phytoplankton may concentrate Al to some extent, the assumption that Al_p is entirely aluminosilicate may result in an under-estimation of the non-detrital fraction, especially during the bloom. Therefore, it is probably safe to guess that nearly all of the particulate Mn and Zn in the water during the latter stages of the bloom is phytoplankton-derived.

The absolute amounts of non-detrital PTM's during March are not known but it is reasonable to guess that they are nonzero since relative to typical sediments or crust the SPM does show some enrichment (EF (Mn) $\sim$ 2, EF (Zn) $\sim$ 5, EF (Cd) $\sim$ 37). Hydrogenous phases may be invoked to explain some of this enrichment, but this is not necessary. Since POC levels are maintained between 150 and 400 μg/l throughout the year (Platt and Irwin, 1968; Sutcliffe, 1972) and since primary productivity during March is usually beginning to increase after the midwinter minimum (Platt, 1971), it is reasoned by analogy with April that much of the non-detrital PTM during March is probably associated with POM. According to Sutcliffe, the ratio of total : living POC varied from 2 - 10 during an annual cycle. Non-living organic detritus has perhaps different amounts of PTM associated with it than living phytoplankton, but this source cannot be neglected in considering PTM forms in oceanic waters (Hirsbrunner and Wangersky, 1976; Wangersky and Gordon, 1965).

The phytoplankton PTM maxima seem to lag behind the peak of chlorophyll a which apparently occured on April 12.

Although the spotty chlorophyll a data leave this observation open to doubt, it suggests that the metals are not absorbed as rapidly at the onset of the bloom as after its peak. Similar observations on the variability of trace metal concentrations in phytoplankton can be cited in support of this (Hayward, 1969; Riley and Roth, 1971). It is thought not unlikely that the accumulation of trace metals by phytoplankton depends on a variety of factors including the stage of growth and ambient levels in the medium.

Trace Metal Cycling in St. Margaret's Bay

It is evident, when Figure 19 is compared with Figures 10 - 13, that the incipient rise of biogenic particulate trace metals coincides with the decline of dissolved trace metals in the water column. Most of the biological fixation apparently occurs between April 2 and April 26. Since Fe is largely present as inorganic SPM, it is not possible to accurately estimate its fixation into biogenic particulate matter, but Figure 19 suggests a maximum of 1 µg/l. This compares well enough with the value of .39 ug/l calculated earlier for its removal. The fixation of particulate Zn appears from Figure 19 to be only about .16 ug/l, which helps to explain why a change in the concentration of dissolved Zn is not visible. The most favorable case is Mn, since changes in both dissolved and particulate forms can actually be determined from the data. The observed decline in dissolved Mn, .78 µg/l, agrees with the corresponding increase manifested by non-detrital particulate Mn, which is 0.7 μg/l. In general, it appears that the biological fixation of Fe, Mn, and Zn estimated either by the observed changes in dissolved or biogenic particulate trace metal concentrations are in essential agreement. Based on the observed uptake of nitrate and assuming a C : N ratio of 7.0, the estimated PTM/C ratios for the bloom are 0.93×10^{-3}, 1.86×10^{-3}, and 0.38×10^{-3} for Fe, Mn, and Zn respectively. These values seem to be somewhat higher than typical of pelagic phytoplankton (Martin and Knauer, 1973), but may not be unusual for phytoplankton grown in coastal waters where dissolved metal concentrations are higher.

Having seen direct evidence of biological control over the concentrations of dissolved trace metals in the rather extreme instance of an intense phytoplankton bloom, it is logical to examine next the significance of the biological cycling of trace metals in St. Margaret's Bay. The primary productivity by phytoplankton in St. Margaret's Bay is 190 ± 60 g C/m^2yr (Platt, 1971). Macrophyte production used to be 603 g C/m^2yr in St. Margaret's Bay (Mann, 1972), but overfishing of the lobster has since allowed the great beds of kelp and seagrasses to be consumed by sea urchins (Mann, pers. comm.; to be published in Helgolander Wissenschaftliche Meeresuntersuchungen). Therefore 190 g C/m^2yr is a fair estimate for gross carbon fixation appropriate to the time of this study, but a certain amount of organic matter and associated nutrients are remineralized within the Bay and must be subtracted from this figure. Before the demise of seaweeds in St. Margaret's Bay, Webster et al (1975) measured the sedimentation rate of organic matter, which amounted to 118 g C/m^{2}yr. This figure balanced the yearly oxygen consumption in the sediments, and because of the shallowness of the water column, was probably a good estimate of remineralization at a time when combined (phytoplankton and macrophyte) yearly production was about 800 g C/m^{2}yr. Hargrave (1973) has shown that oxygen consumption can be empirically described as a function of primary productivity and mixed-layer depth. This relationship allows an estimate to be made of the carbon equivalent of oxygen uptake for the sediments in St. Margaret's Bay. The net photosynthetic fixation of carbon thus derived is 130 g C/m^{2}yr, i.e. one third of the total production by phytoplankton is oxidized in the bay. Using the inferred PTM/C ratios, the yearly removal of Fe, Mn, and Zn are calculated to be 121, 242, and 50 mg/m^{2}yr, respectively. Given the mean residence time of water for the entire Bay (19.5 days, calculated from the data of Heath, 1973) and further assuming that the Bay is well mixed and that concentration averages for March and April are representative of the entire year, the relative residence times of the metals can be calculated. The equation for the relative residence time is $T_M' = T_M/T_{H_2O} = ØM/(ØM + B)$, where Ø is the flux of water, M the average concentration of dissolved metal, and B the flux of biological removal. The relative residence time is an inherent parameter of the particular element in the aquatic system under consideration, and is a measure of that element's tendency to depart from conservative behaviour by whatever mechanism, chemical or biological. Since the residence time for transition metals in the oceans is $10^2 - 10^4$ years, it is expected that biological removal far outweighs chemical removal in St. Margaret's Bay. The flux data and relative residence times are tabulated below.

	B	Φ_M	$T_{M'}$
Fe	121 mg/m^{2}yr	332 mg/m^{2}yr	.73
Mn	242	795	.77
Zn	50	532	.91

These results indicate that in spite of the rapid renewal of water in the bay, the removal of dissolved Fe, Mn, and Zn by biological activity is quantitatively important. For example, if the average concentration of Fe were the same offshore as it is in St. Margaret's Bay, and if there were no input of Fe from fresh water, the outflowing water from the Bay would be depleted by 45%. Of course, river input is significant for all three metals, as noted previously. A rough estimate of river concentrations can be derived from the salinity dependence of metal concentrations in the surface layer. The riverine inputs are then calculated by multiplying the river concentrations by the mean fresh water inflow of 12.4 m^3/m^{2}yr (Heath, 1973). In order to achieve a final balance between inputs and outputs, it is necessary that the shelf water be depleted in Fe, Mn, and Zn relative to the water in the Bay by 58%, 15%, and 53% respectively. It is to be expected that shelf waters will have lower concentrations than Bay waters which receive more runoff, and the extent to which this is true may be different for various trace metals. Calculations of this type are usually subject to considerable uncertainty; it would be better to have measured inputs as well as outputs so that the net balance could be checked for internal consistency.

The mid-depth minimum feature observed in the profiles of Fe and Mn may be maintained by a diffusive flux of these metals from the sediments. Whether this mechanism is physically reasonable can be examined in two ways. If benthic regeneration of organic matter, which amounts to 60 g C/m^{2}yr is the only source, then the calculated fluxes of Fe and Mn are .019 ug/cm^{2}day and .038 µg/cm^{2}day respectively. The resulting doubling times in the lower water column (10 m), are comparable to the residence time of the water, so this hypothesis does seem reasonable. But can these fluxes account for the magnitude of the observed concentration differences at 25 and 40 meters? The average concentration differences are .05 µg/l for Fe and .14 ug/l for Mn. If the eddy diffusivity of the lower mixed layer is about 10 cm^2/sec in March (a reasonable estimate based on tidal currents), these gradients imply a flux of .028 µg/cm^{2}day for Fe and .081 µg/cm^{2}day for Mn. Considering the uncertainties in the eddy diffusivity and flux of organic carbon, it is felt that there is essential agreement between the two sets of calculated fluxes. Therefore, there probably is enough Fe and Mn regenerating in the sediments and diffusing into bottom waters to maintain the observed concentration gradients in steady state. The fact that no such feature is obvious in the profile of Zn is also in agreement with prediction.

Diagenetic remobilization of trace metals in estuarine sediments is supported by two other lines of evidence. Presley et al (1972) found from one to several orders of magnitude enrichment of Fe, Mn and Zn in the interstitial water of sediments from Saanich Inlet, British Columbia. The highest concentrations were attained by Mn, and smaller enrichments (less than a factor of ten) were observed for several other transition elements. They felt that organic complexing was at least partly responsible for causing the enrichments. Elderfield and Hepworth (1975) showed that sediment diagenesis can cause the enrichment of certain metals at the sediment surface, and calculated fluxes for several metals in the Conway and Tees Estuaries. It seems likely that the diagenetic fluxes of metals in the estuaries just mentioned are balanced by the input of organic matter and associated trace elements. Rowe et al (1975) suggested that benthic nutrient regeneration plays a major role in the high productivity of coastal and estuarine waters. Therefore, remineralization of biogenic PTM's in the sediments may be an important part in the cycle of trace metals in productive coastal waters.

Concerning the non-conservative behaviour of Mn in St. Margaret's Bay, an interesting comparison can be made with Narragansett Bay (Graham et al, 1976). Narragansett Bay is shallower (10 m), more estuarine (24 - 32‰ salinity), and dissolved Mn is present at higher concentrations (up to 60 µg/l), although the residence time of water is similar (about one month) compared to St. Margaret's Bay. The interesting observation made by Graham et al. (1976) is that although total Mn is quite conservative in Narragansett Bay, dissolved Mn is not. Surface waters (1 m) are depleted in dissolved Mn relative to deep waters (11 m), with respect to the conservative mixing line drawn between river and deep water. The flux of Mn from the sediments was determined by measuring the rate of accumulation of Mn in open bottomed PVC chambers placed on the sediment surface. The average value obtained was about 2 µg/cm^2·day, which is almost two orders of magnitude higher than St. Margaret's Bay and probably sufficient to explain the difference between surface and deep dissolved Mn in Narragansett Bay. The authors believed that oxidation of Mn^{2+} to particulate MnO_2 was responsible for the non-conservative effects. They did not consider the possibility of biological uptake and regeneration.

Although uptake by phytoplankton seems to [illegible]e the most probable explanation for the non-conservative changes observed in St. Margaret's Bay, it is not the only possible explanation for such behaviour. In fact, the real situation in St. Margaret's Bay may be considerably more complex. The chemical mechanisms that remove trace metals from the ocean are not well understood, and the possibilities are numerous: 1) uptake by living phytoplankton analogous to P and N, 2) uptake into phytoplankton tests analogous to Si, Ca, and Sr, 3) authigenic formation by involvement in the DOC ⇆ POC equilibrium, 4) adsorption onto particulate surfaces, e.g. clays, tests, living and detrital organic matter, etc., 5) precipitation of an insoluble inorganic phase such as $Fe(OH)_3$ or MnO_2, 6) any combination of the above. The conclusions reached about the nonconservative behaviour of trace metals in St. Margaret's Bay would probably not be substantially altered by the choice of mechanism.

In summary, the concentrations of dissolved Fe, Mn, Cu, and Zn reflect sporadic inputs of fresh water to the surface layer. The deeper water is less subject to fluctuations caused by local conditions but is affected by advection of oceanic water. Iron and Mn display concentration minima in their profiles while Cu and Zn do not. That much of the SPM in St. Margaret's Bay is resuspended bottom sediments is indicated by the profiles of particulate Fe and Al. Variations of particulate Mn, Zn, and Cd with time and depth indicate that these metals are partly associated with aluminosilicates and partly with particulate organic matter. During the phytoplankton bloom, dissolved trace metals are converted into particulate trace metals; the depletion of dissolved Fe and Mn is obvious and mirrors that of nitrate. Corresponding changes are observed in the particulate fraction; Mn and Zn apparently become almost entirely biogenous. The nonconservative changes in Fe, Mn, and Zn are keyed to a model of primary production, and the conclusion is drawn that much of the stream-introduced metals are removed from St. Margaret's

Bay by biological production. The inflected profiles of Fe and Mn suggest that these metals diffuse from the sediments; this is supported by the estimated benthic regeneration required by the model.

Conclusions

The major conclusions of this thesis may be summarized as follows. 1) Transition metal distributions in coastal seas are nonconservative. The major cause of nonconservative behaviour is probably biological, but chemical processes may be important as well. The time scale of removal in both areas investigated would imply that nonconservative distributions are a normal feature of the oceans. Therefore, the ocean does contain inherent trace metal variability over rather short scales of distance and time. 2) Chemical fractionation of dissolved transition metal species in aerosol particles produced by bubbles bursting at sea does occur. Iron and Cu exist partly as organic colloids in coastal seawater, and it is these species which are responsible for chemical fractionation. That chemical fractionation alone is responsible for the high concentrations of these elements in the marine atmosphere is very improbable. The ocean is rather a sink for transition and heavy elements in the atmosphere; in fact, the main flux of some elements to the open sea may be via the atmosphere.

The major questions raised by this thesis may be summarized as follows. 1) What are the chemical mechanisms responsible for removing transition metals from coastal waters? Are they primarily biological (uptake by phytoplankton) or chemical (adsorption and precipitation onto particle surfaces)? Since the means by which metals are removed governs their fate, important clues can sometimes be obtained from oceanic distributions. More sophisticated analytical techniques are also needed for studying suspended particulate matter which are designed to separate trace metals into lithogenous, hydrogenous, and biogenous fractions. 2) Are transition metal colloids in seawater truly metal-organic coordination complexes or are they something else? Do they result from autochthonous (e.g. biological production and decay), or allochthonous processes (e.g. metal-organic colloids introduced by rivers)? Are transition metals strongly organophilic in the marine environment? In the author's opinion, the question of biologically mediated interactions between PTM and POC and between DTM and DOC is still unresolved.

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Appendix

The Methods of Analyzing Samples for Trace Metal Content

The technique used for analyzing dissolved Fe, Mn Cu, and Zn is an eclectic modification of methods which have described (Brooks et al, 1967; Brewer et al, 1969; Nix and Goodwin, 1970; Kremling and Petersen, 1974). It consists on a solvent extraction step using sodium diethyl-dithiocarbamate (NaDDC) and methyl-isobutyl ketone (MIBK) followed by injection of the extract directly into the heated graphite analyzer (HGA-70) of an atomic absorption spectrophotometer (PE-403). Each sample is divided into four 50 ml aliquots and standard additions are made to the aliquots. The concentration of NaDDC used is 1000 times in excess of the total extractable metal content of the sample, i.e. 3.5×10^{-3} M. The final extract is approximately 25 times more concentrated in the metals than seawater.

Since NaDDC is unstable in acid solution, its decomposition products buffer the solution, raising the seawater pH from 3 to 7. When additional buffering capacity was needed, HCO_3^- or $H_2PO_4^{2-}$ were sometimes used. To avoid introducing large acid blanks, natural samples are acidified only to pH 3. The samples were found to be stable at that pH for at least one month. The NaDDC solution (and any buffer, if used) are pre-extracted with MIBK. The MIBK was redistilled in a Pyrex still. Pyrex separatory funnels and Quickfit sample tubes must be soaked in concentrated nitric acid and pre-extracted with NaDDC/MIBK. To avoid adventitious contamination, glassware and pipettes were kept under a polyethylene film cover when not in use.

After the entire suite of samples from the Gulf of St. Lawrence had been analyzed, the analytical precision was calculated from the results. This was done by first estimating the variance of a single aliquot. Since each sample is determined from four aliquots, the sample estimate is calculated from the formula, $(\mathrm{ERMS})^2 = \sum_{i=1}^{4}(y_i - \tilde{y}_i)^2/(n - 2)$, where y is an aliquot's absorbance and $n = 4$. The pooled estimate of the variance is $\sigma^2 \doteq 2((\mathrm{ERMS}_1)^2 + (\mathrm{ERMS}_2)^2 + \cdots + (\mathrm{ERMS}_k)^2)/3k$ which is taken to be equal to σ^2 since $k = 38$. An estimate of the variance of the analytical concentration is then calculated from the formula, $\mathrm{var}(a/b) = (\sigma^2/b^2)(1/n + y^2/(b^2\sum(x_i^i - x_i)^2))$ where $n = 4$; y and x are absorbance and concentration respectively; b and a are slope and intercept respectively (Bennett and Franklin, 1954). The coefficients of variation for the elements are: Fe 7.6%; Mn 9.9%; Cu 7.2%; and Zn 6.7%. These figures are slightly optimistic since they represent the best case where the standard addition is 2/3 of the sample's concentration. The error estimates for fractionation factors were also calculated from formulae based on the principles given by Bennett and Franklin (1954).

The validity of measuring the sample blank is open to question since the medium used in place of sample (e.g. deionized water) may contain some trace metals. The lowest blanks obtained for the entire proceedure using either deionized water or artificial seawater passed through a column on Chelex 100 are: Fe .09; Mn < .005; Cu .04; and

Zn .02 (µg/l). These values were not subtracted from the data. Exposure of eleven randomly picked samples to ultraviolet light in quartz tubes in the manner described by Armstrong et al (1966), produced no apparent enhancements No effect was observed even when the amount of NaDDC was reduced to 1/500 of the normal dose. Therefore, it is believed that the values reported are reasonably accurate and represent total dissolved trace metal content of the seawater samples.

The analysis of particulate trace metals essentially follows the procedure of Wallace and Duce (1975). The filters are placed in Teflon dishes and ashed in an International Plasma Corporation low temperature asher. The residue is dissolved in 20 µl of concentrated HF and 20 µl of concentrated HCl, diluted as necessary for Al, Fe, Mn, Zn, and Cd determinations and measured against standards prepared in the same matrix with the heated graphite analyzer. Copper was not determined because preliminary trials were unsatisfactory. Blanks for this procedure were usually less than 10%. Precision for particulate trace metals was not calculated, but is thought to be $\lesssim$ 10%.

X-ray diffraction analysis was performed on some of the filters from the Gulf of St. Lawrence before chemical analysis by mounting them unaltered on glass slides. The peaks were visible enough using maximum sensitivity of the instrument to enable a qualitative estimate of the suite of minerals present.

Table 8 The total fluxes of elements to the oceans from congruent crustal weathering, via rivers, and from the atmosphere. Fluxes are in units of 10^6 kg per year.

	Congruent Weathering	Rivers	N. Sea, (diss.)	Bermuda, total	Phytoplankton uptake
Cl	230,000				
Na	190,000				
Mg	75,000				
Ca	120,000				
K	58,000				
SO_4	290,000				
HCO_3	340,000				
Si	720,000				
Al	210,000	12,000	17,000	15,000	8,000
Fe	140,000	21,000	15,000	11,000	40,000
Sc	56	0.1	0.9		
V	340	29	870	18*	2,000
Cr	250	32	300	110	400
Mn	2,400	224	1,700	170	800
Co	64	6	40		
Ni	190	10	540	9	400
Cu	140	224	3,800	36	800
Zn	180	640	23,000	94	2,000
As	5	64	980	4**	
Se	0.1	6	54	5**	
Ag	0.2	9			40
Cd	0.5		160	7	80
Sb	0.5	3	140	10**	
Hg	0.2	2		22**	8
Pb	32	96	4,900	130	800

* Duce and Hoffman (1976), ** Duce et al (1976) and assuming a total deposition velocity of 0.3 cm/s.

Congruent weathering was derived from the average

Table 8, continued

crustal abundances of Taylor (1964) and assuming 2.54 x 10^{12} kg of crust dissolved per year (120 ppm dissolved solids, Livingstone (1963)). The parallel estimates of river fluxes are those of Turekian (1971) which he based on a compilation of literature values of measured concentrations in rivers. The two estimates of atmospheric deposition were calculated as follows: The fluxes of the North Sea estimate are those of Cambray (1974) scaled to the area 3.6 x 10^{18} cm^2. The same approach is used for the estimate based on atmospheric fluxes into the Sargasso Sea (Wallace et al, 1976). Uptake by phytoplankton was calculated from the data of Martin and Knauer (1973) assuming an annual world oceanic production of 2 x 10^{10} tons of organic carbon per year.

Table 9

Data for the Gulf of St. Lawrence. Trace Metals are µg/l. Nutrients are µg-at./l.

Sta.	Salinity	SiO_4	PO_4	NO_3	Fe_d	Mn_d	Cu_d	Zn_d	Fe_p	Mn_p	Zn_p
01	30.07	.34	.54	-.01	1.1	.92	.68	-	1.7	.16	.067
04	30.29	1.24	.71	1.23	.49	1.2	.35	.32	3.8	.33	.050
06	31.14	.43	.75	.08	1.1	.73	.40	.32	.84	.074	.039
09	31.37	.61	.91	.34	.60	.60	.39	.63	.48	.014	.031
12	29.84	1.14	.44	.31	1.9	1.0	.28	.66	2.3	.032	.052
13	27.31	4.28	.32	.45	1.5	1.2	.26	.50	4.3	.099	.043
18	28.11	4.19	.40	1.25	2.6	1.4	.27	.52	6.9	.46	.079
19	30.85	.25	.36	.08	.87	.42	.32	.35	1.1	.020	.023
20	31.16	.51	.45	.04	.39	.49	.50	.60	.36	.019	.041
21	31.15	.25	.45	.18	.46	.50	.31	.71	.24	.013	.022
22	31.32	.25	.37	-.06	.20	.27	.28	.39	.12	.007	.016
23	31.37	.60	.39	-.06	.27	.30	.33	.38	.14	.010	.014
24	31.13	.51	.47	.04	.34	.79	.46	.69	.26	.039	.076
26	29.99	2.18	.55	.95	.70	1.0	.32	.69	1.9	.11	.084
27	29.97	4.47	.60	2.95	1.5	1.5	.43	1.4	6.8	.17	.090
29	29.68	4.76	.53	2.22	1.2	2.3	.43	.98	4.3	.12	.060

Table 9

Sta.	Salinity	SiO_4	PO_4	NO_3	Fe_d	Mn_d	Cu_d	Zn_d	Fe_p	Mn_p	Zn_p
30	30.72	1.23	.56	.47	.28	.77	.38	.57	1.2	.069	.034
35	31.17	.46	.31	.35	.23	.59	.39	1.0	.93	.064	.043
36	30.55	1.23	.19	.23	.52	.87	.52	1.0	.90	.088	.035
37	26.27	21.98	.71	11.90	4.3	3.3	.55	1.1	44.	.78	.29
38	26.39	20.31	.68	7.00	3.0	2.6	.39	.82	12.	.24	.17
39	27.31	4.20	.44	1.58	1.8	1.6	.32	.59	7.0	.16	.060
40	29.00	1.93	.60	.28	1.2	2.1	.30	.32	2.7	.072	.037
41	28.31	1.31	.44	1.53	3.8	1.8	.30	.62	9.9	.20	.099
42	26.11	17.23	.44	10.26	3.1	3.0	.51	1.2	33.	.60	.21
43	24.80	18.33	.91	9.76	4.7	2.5	.53	1.1	13.	.31	.16
44	21.87	19.97	.87	10.41	5.2	2.6	.72	1.2	103.	1.4	.51
45	20.82	21.37	.87	10.06	6.4	4.5	.71	1.5	100.	1.2	.51
46	21.92	19.97	.86	9.66	6.2	2.9	.62	1.2	44.	.66	.30
47	26.58	16.30	.80	10.56	3.0	2.6	.48	1.1	24.	.43	.21
48	27.89	14.54	1.03	9.41	2.7	2.2	.46	.87	23.	.43	.14
49	27.30	13.98	.98	8.65	1.8	2.7	.48	.94	17.	.38	.11
50	26.24	14.38	.86	7.74	1.7	2.7	.47	.99	9.9	.24	.094

Table 9

Sta.	Salinity	SiO_4	PO_4	NO_3	Fe_d	Mn_d	Cu_d	Zn_d	Fe_p	Mn_p	Zn_p
51	27.27	10.93	.85	4.81	2.1	2.2	.55	.79	1.1	.041	.022
52	27.77	.37	.98	.07	1.1	3.4	.50	.71	.57	.27	.036
53	30.27	.37	.37	.07	.43	.99	.36	.67	.26	.033	.022
54	–	1.97	.42	.07	1.5	4.8	.38	1.1	2.5	.17	.030
55	28.31	2.45	.53	.07	1.1	4.4	.45	.69	6.8	1.5	.067

Table 10

Data for St. Margaret's Bay. Sample depths are 1, 5, 10, 25, and 40 metres.

	M 2	M 9	M 16	M 23	M 26	A 2	A 5	A 12	A 15	A 26	Ma 9
Fe_d	.77	.72	1.5	1.3	.68	.76	.76	.41	.28	.37	.97
μg/l	.86	.67	.83	.96	.46	.70	.69	.41	.30	.43	.84
	.57	.72	.54	.45	.44	.59	.42	.37	.29	.21	.55
	.38	.49	.48	.40	.38	.44	.44	.20	.13	.17	.37
	.34	.60	.66	.47	.46	.54	.58	.28	.088	.19	.27
Mn_d	1.5	.99	2.8	4.7	1.8	2.3	2.0	1.4	1.6	1.1	2.7
μg/l	1.8	.89	1.0	3.2	1.2	2.3	2.1	1.5	1.3	1.1	2.3
	1.1	.88	.79	.91	1.1	2.0	1.0	1.2	1.0	.58	1.9
	.44	.51	.38	.65	.48	.83	.77	.52	.72	.39	1.5
	.46	.85	.47	.68	.75	1.1	1.0	.76	.56	.54	1.6
Cu_d	.24	.27	.30	.34	.31	.25	.23	.19	.22	.29	.20
μg/l	.22	.23	.20	.24	.20	.17	.22	.19	.16	.23	.17
	.19	.25	.20	.19	.16	.20	.18	.16	.19	.21	.14
	.16	.23	.18	.18	.17	.17	.30	.16	.21	.21	.10
	.15	.22	.17	.17	.17	.18	.30	.21	.17	.41	.14
Zn_d	1.1	.65	.97	1.1	2.2	1.3	1.3	1.1	1.6	1.3	1.2
μg/l	.90	.45	.49	.68	1.3	1.6	1.1	1.1	.80	.90	.71

Table 10

	M 2	M 9	M 16	M 23	M 26	A 2	A 5	A 12	A 15	A 26	Ma 9
Zn_d	.58	.55	.38	.44	1.0	.75	.74	.84	.82	.85	.57
µg/l	.61	.40	.31	.36	.84	.53	1.9	.82	.62	1.0	.54
	1.0	.37	.31	.31	.78	.53	2.6	1.1	.77	2.5	.82
S. %	30.78	31.32	30.28	29.83	30.89	30.81	30.78	30.81	30.93	30.66	30.23
	-	31.38	31.03	30.15	31.06	30.80	30.76	30.83	31.05	30.66	-
	31.12	31.38	31.29	31.16	31.13	-	31.27	30.92	31.12	31.03	30.88
	31.15	31.65	31.51	31.37	31.38	31.39	31.35	-	31.39	-	31.67
	31.79	31.81	31.63	31.50	31.53	31.42	31.61	31.61	31.55	31.48	31.54
NO_3	-	-	5.1	4.1	3.7	7.9	2.6	-	.72	.52	1.4
µg-at/l	5.7	6.2	9.8	4.7	4.6	6.1	4.4	-	.47	.43	2.8
	5.3	5.3	9.1	7.7	5.8	7.0	2.6	.25	.78	.83	.54
	6.6	6.2	7.2	4.8	4.7	6.2	-	4.2	-	1.6	1.4
	7.2	8.3	6.0	5.4	6.1	6.8	8.0	5.0	4.9	4.5	2.2
Fe_p	7.5	6.4	7.0	18.	11.	6.2	5.0	-	8.4	5.4	3.8
µg/l	7.5	6.4	9.6	13.	12.	6.0	6.4	-	9.1	-	3.2
	8.1	7.4	10.	12.	11.	7.9	6.1	8.0	10.	3.9	3.2
	14.	13.	11.	15.	12.	-	7.8	16.	14.	4.5	4.2
	19.	18.	~15.	23.	17.	15.	16.	25.	17.	10.	6.8

Table 10

	M 2	M 9	M 16	M 23	M 26	A 2	A 5	A 12	A 15	A 26	Ma 9
Mn_p	.40	.37	.24	.71	.49	.57	.53	–	.77	1.5	.44
μg/l	.43	.32	.39	.45	.50	.51	.64	–	.67	–	.44
	.43	.39	.46	.56	.52	.66	.51	.74	.84	1.1	.55
	.58	.52	.48	.78	.53	–	.58	.92	.85	1.1	.73
	.59	.57	.63	1.0	.61	.73	.69	.89	.82	1.0	.82
Zn_p	.065	.025	.040	.150	.053	.021	.040	–	.22	.12	.041
μg/l	.042	.079	.040	.160	.067	.026	.051	–	.16	–	.032
	.095	.022	.165	.073	.075	.071	.084	.091	.15	.14	.073
	.10	.078	.069	.072	.085	–	.049	.13	.22	.12	.049
	.20	.20	.073	.11	.064	.036	.089	.27	.19	.44	.036
Cd_p	1.7	.42	1.4	2.4	1.0	1.6	.91	–	1.6	.48	1.3
ng/l	.65	1.3	.86	2.8	1.4	1.4	1.2	–	1.8	–	.79
	.62	1.2	.42	1.3	1.6	1.3	.94	1.3	4.6	1.4	.61
	1.3	1.3	1.0	2.1	1.7	–	.60	2.3	1.6	.99	1.9
	3.6	.90	1.4	2.0	1.2	1.7	1.6	2.8	2.1	.75	.33
Al_p	9.4	8.4	8.1	25.	16.	6.4	6.3	–	9.8	4.6	2.0
μg/l	9.1	8.8	11.	17.	17.	6.7	7.9	–	12.	–	2.1

Table 10

	M 2	M 9	M 16	M 23	M 26	A 2	A 5	A 12	A 15	A 26	Ma 9
Al_p	8.6	12.	12.	18.	16.	11.	7.3	9.5	13.	3.3	2.8
µg/l	17.	22.	13.	21.	19.	-	12.	22.	19.	5.4	4.6
	30.	23.	17.	28.	27.	25.	24.	22.	25.	14.	8.7
SPM	1.2	.91	1.4	1.3	1.1	.85	.86	-	1.3	.71	.48
mg/l	.64	1.9	.93	2.5	2.2	1.1	1.1	-	2.4	-	.40
	1.2	.59	1.2	1.8	1.0	.85	1.8	1.6	2.0	.78	.39
	1.7	.83	.83	1.6	1.5	-	.85	1.1	1.7	.49	.29
	1.0	2.2	2.2	1.7	1.7	1.2	1.5	1.6	1.2	1.0	.88
Chl. a	-	.45	.53	.56	.94	.83	.83	-	3.78	.56	-
µg/l	-	.51	.57	.82	1.03	.83	.84	-	7.27	.48	-
	-	.46	.54	.56	.68	.53	1.52	-	8.14	.59	-
	-	.54	.51	.53	.36	.48	2.01	-	2.47	.78	-
	-	.17	.50	.49	.3	.42	.19	-	1.29	.78	-