

Manganese, nickel, zinc and cadmium distributions at the Fram 3 and Cesar ice camps in the Arctic Ocean

Trace metals
Fram 3
Cesar
Arctic

Métaux-trace
Fram 3
César
Arctique

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ABSTRACT

Manganese, nickel, zinc and cadmium concentrations have been measured in water samples collected at the Fram 3 and Cesar ice stations in the Arctic Ocean. Metal distributions at these stations are compared to other measurements of Arctic Ocean metal concentrations. The surface waters at Fram 3 have lower trace metal concentrations than do those at Cesar but Atlantic layer and deep water concentrations at the two locations are similar. The most interesting feature of the Cesar distributions is a distinct Cd and Ni maximum coincident with the nutrient maximum. A coincident manganese maximum is not observed. Comparison of the metal levels in this maximum with metal (and Si) levels in the surface waters of the Bering Sea would suggest that surface waters from the Bering Sea are the source of the elevated metal concentrations.

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RÉSUMÉ

Répartitions du manganèse, du nickel, du zinc et du cadmium aux stations glaciologiques Fram 3 et César dans l'Océan Arctique

Le manganèse, le nickel, le zinc et le cadmium ont été dosés dans des échantillons d'eau prélevés à l'emplacement des stations glaciologiques Fram 3 et César, situées dans l'Océan Arctique. La répartition des concentrations métalliques dans ces stations est comparée aux valeurs des concentrations métalliques mesurées en d'autres stations de l'Océan Arctique. A la station Fram 3, les eaux de surface sont caractérisées par des concentrations d'oligo-éléments métalliques plus faibles que celles de la station César, mais dans ces deux sites, les concentrations caractérisant la couche d'eau de l'Atlantique et les eaux profondes sont similaires. Le détail le plus intéressant des répartitions observées à l'emplacement de la station César est un maximum perceptible des concentrations de Cd et Ni, qui coïncide avec la concentration maximale des éléments nutritifs. On n'observe pas de coïncidence des maxima des concentrations de manganèse. Si l'on compare les concentrations métalliques caractérisant ce maximum aux concentrations métalliques (et de Si) relevées dans les eaux de surface de la mer de Béring, les résultats obtenus suggèrent que les eaux superficielles en provenance de la Mer de Béring sont à l'origine des concentrations métalliques élevées.

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INTRODUCTION

The past few years have seen a marked increase in the amount of chemical oceanographic activity in the Arctic Ocean. This activity has included several studies of trace metal distributions. The first of these was the

determination of vertical zinc, cadmium, copper, aluminium and iron distributions at the Lorex ice station in the central Arctic Ocean (Moore, 1981; 1983). Subsequently, profiles for lead, cadmium, copper, nickel, iron and zinc, based on the Ymer 80 expedition have been reported (Danielsson, Westerlund, 1983; Mart *et al.*,

1983; 1984). Other studies, such as Erickson (1983), have concentrated on shelf areas.

In 1981, seawater samples for trace metal analysis were collected for me at the Fram 3 drifting ice station and in 1983 samples were also collected at the Cesar (Canadian Expedition to Study the Alpha Ridge) ice station. In this paper I will present the results from these determinations and make comparisons with other results from the Arctic Ocean.

EXPERIMENTAL PROCEDURES

The samples at both stations were collected with 5 l teflon-coated Go-Flo sampling bottles modified for collection of samples for trace metals and deployed on Kevlar hydrowire. The general validity of this sampling technique has been well documented (Bruland *et al.*, 1979; Bowers, Windom, 1982). Sampling from the ice, however, presents some rather different problems. In some respects the ice island may be "cleaner" than a ship but there may be problems associated with sampling over extended periods from the same hydro-hole. The preparation of samplers and processing of subsamples in a temporary hut on the ice may also give rise to unusual contamination problems. In both experiments the single vertical profiles being reported here were constructed from samples collected over fairly long periods. The two sampling locations are shown in Figure 1. The sampling at Fram 3 ($\sim 82^{\circ}\text{N}$, 6°E) took 10 days during which time the station drifted approximately 90 km. The water depths decreased from 3 700 to 800 m during this period. Likewise, at Cesar (86°N , 111°W) sampling took 20 days while drifting about 75 km. The water depths at Cesar varied between 1 200 and 1 700 m and were $\sim 1 350$ m when my deepest samples were collected. In both cases, the trace metal samples were collected in conjunction with sampling for nutrient/alkalinity studies (Anderson, Jones, 1986; Jones, Anderson, 1986). Further details of station loca-

tions and sampling procedures as well as salinity and nutrient results can be found in these references.

The samples collected at Fram were unfiltered. The samples were drained directly from the Go-Flos into 2 l conventional polyethylene bottles and acidified with 5 ml of Ultrex HCl. At Cesar the samples were filtered by pressurizing the Go-Flos and forcing the samples through $0.4 \mu\text{m}$ Nuclepore filters in polypropylene filter holders (the filters and holders were precleaned and preloaded at BIO).

Sample analysis was conducted in a clean room laboratory. The samples were concentrated by complexation with oxine immobilized on silica gel columns and eluted with dilute HCl/HNO₃ (Sturgeon *et al.*, 1981). Analysis was done by graphite furnace atomic absorption spectrophotometry using a Perkin Elmer 5 000/500 system. Accuracy of the results was determined by analysis of NASS-1 seawater standard (Berman *et al.*, 1983). Analytical precision determined by analysis of replicates and accuracy by comparison to NASS-1 are $< 10\%$ for all metals.

RESULTS

The metal results for samples from Fram 3 and Cesar are shown in Figures 2-5. The Fram station was north of Spitzbergen in the Transpolar Drift stream of surface water flowing out of the Arctic Ocean. The deeper samples were collected in the inflowing Atlantic and bottom waters reasonably close to the region where they enter the Arctic basin. Sampling from the Ymer 80 expedition (Danielsson, Westerlund, 1983; Mart *et al.*, 1984), although covering a much wider area, should have been from waters having fairly similar characteristics to those at Fram. The samples from the Cesar expedition were collected in the Canadian basin over the Alpha ridge. Surface samples from this station would have been collected in the Beaufort Sea gyre. Water characteristics were very similar to those at

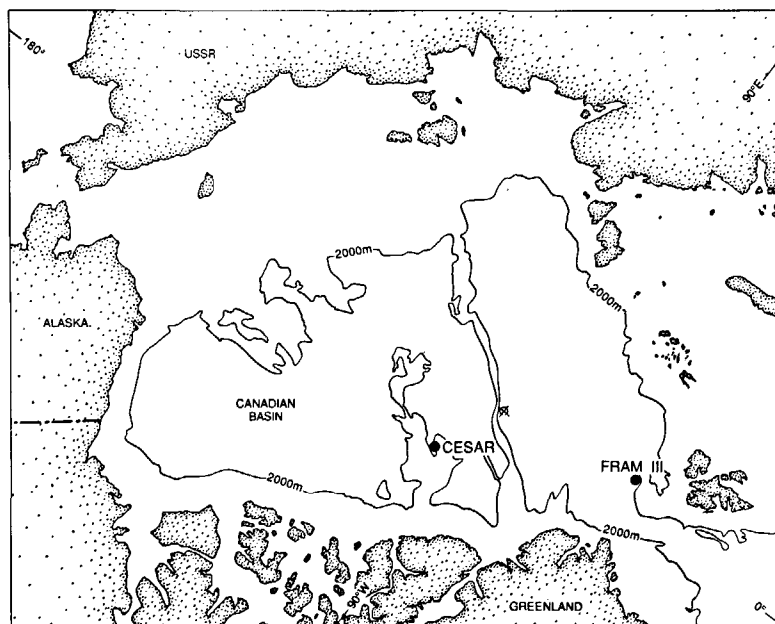


Figure 1
Map of Arctic Ocean showing station locations.

Table

Trace metal concentrations in Arctic Ocean water layers (nanomoles per litre).

Metal	Layer	Fram 3	Cesar	Ymer 80 ¹	Ymer 80 ²	Loxex ³
Cd	Surface layer	0.16±0.06 (6)*	0.48±0.06 (3)	0.09	0.15	0.31
	Nutrient max.		0.62±0.14 (3)			0.58
	Atlantic layer	0.21±0.01 (4)	0.26±0.06 (6)	0.14	0.18	0.19
	Deep water	0.27±0.06 (5)	0.23±0.05 (5)	0.14	0.22	0.18
Ni	Surface layer	3.8±0.3 (6)	5.2±0.1 (2)	2.3	3.4	
	Nutrient max.		6.3±1.2 (3)			
	Atlantic layer	4.0±0.4 (4)	3.0±0.4 (6)	2.1	3.5	
	Deep water	4.1±0.4 (4)	2.8±0.3 (5)	3.2	3.6	
Zn	Surface layer	1.0±0.3 (3)	2.7 (1)		1	2.9
	Nutrient max.		5.7±1.2 (3)			5.5
	Atlantic layer	3.8±0.7 (3)	4.7±0.7 (6)		1.5	3.1
	Deep water	4.1±0.9 (4)	3.5±1.5 (5)		3.5	2.6
Mn	Surface layer	4.7±1.1 (6)	2.0±0.4 (3)			
	Nutrient max.		1.0±0.3 (3)			
	Atlantic layer	2.7±0.7 (4)	0.42±0.18 (6)			
	Deep water	4.3±1.7 (4)	0.63±0.18 (5)			

* Arithmetic mean ± standard deviation (number of samples).

¹ Mart *et al.*, 1984.² Danielsson, Westerlund, 1983.³ Moore, 1981.

Loxex (Moore, 1981). The trace metal concentrations in these water layers (means and standard deviations) for both of the expeditions are listed in the Table. The samples assigned to the deep water layer at Fram 3 include samples from much greater depths than the deep water samples from Cesar. This difference in sampling depths contributes to the observed differences in average concentrations in the deep layers at the two locations. Average concentrations from the Ymer 80 (Danielsson, Westerlund, 1983; Mart *et al.*, 1984) and Loxex (Moore, 1981) expeditions are included for comparison purposes.

It is important to point out that there is more scatter than would be expected based on the stated laboratory precision of ~10% for each element. This scatter is most clearly evident in the surface samples for Fram 3. The top 60 m of the water column has uniform salinity and temperature and would probably be expected to have fairly uniform metal concentrations, but only nickel shows uniform concentrations in this layer. It is not possible to conclusively show whether this imprecision is caused by contamination during sampling or real variability. It should be noted, however, that the sampling at each "station" took many days and the station drifted by as much as 90 km. This aspect of the sampling may have meant that there was more real variability in metal concentrations than would have been expected for a more traditional oceanographic sampling station. Nevertheless, the actual observed precision for groups of samples that should have had uniform characteristics was 20-25% (except for Ni where it was 10%) rather than the 10% expected from laboratory precision.

The cadmium profiles from Fram 3 and Cesar are illustrated in Figure 2. The Cesar profile is very similar to the Cd profile already reported for Loxex (Moore, 1981), and the Fram 3 data agree very well with that from Ymer 80 (Danielsson, Westerlund, 1983; Mart *et al.*, 1984). It is evident from this figure that the Cd concentration in surface water in the Canadian basin (Loxex and Cesar) and the Eurasian basin (Ymer and

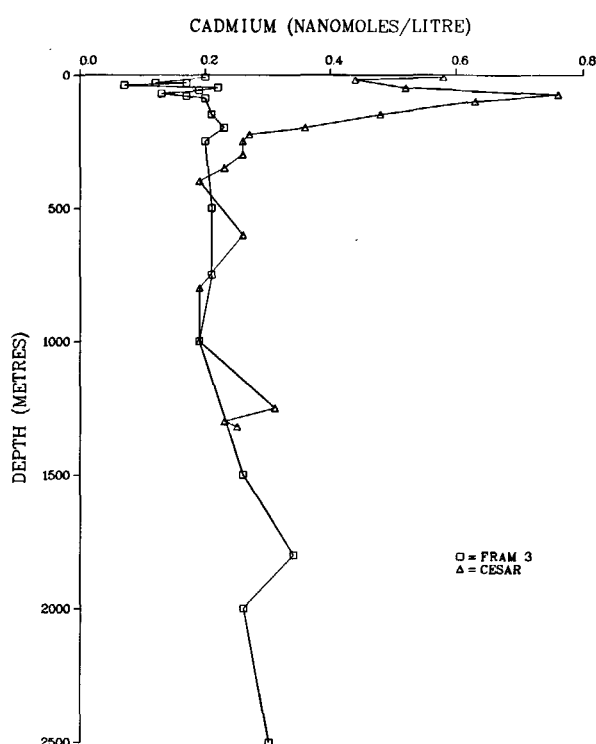


Figure 2
Cadmium profiles for Fram 3 and Cesar.

Fram) are quite different. Not only are the very near surface levels in the Canadian basin higher but there is a very striking anomaly at 100 m. Below about 400 m the various profiles are indistinguishable.

The feature at 100 m in the Canadian basin is strongly correlated with very pronounced nutrient maxima. The nutrient maxima were originally thought to simply reflect advection of Bering Sea water, high in nutrients, into the Arctic Ocean (Kinney *et al.*, 1970). The cadmium signal was attributed by Moore (1981) to the same advective process. Indeed the salinity, cadmium and silica concentrations at Loxex [and Cesar] closely resemble those found in surface water at Geosecs station 219 in the Bering Sea (Boyle *et al.*, 1976). More

recent work based on the interpretation of nutrients and alkalinity data, however, has suggested that processes of ice formation and brine rejection, which seem likely to be responsible for the maintenance of the halocline (Aagaard *et al.*, 1981; Melling, Lewis, 1982), together with diagenetic processes on the shelves may play a major role in the formation of the characteristics of water at the nutrient maximum (Moore *et al.*, 1983; Jones, Anderson, 1986).

The nickel results from Fram 3 (Fig. 3) agree very well with those from the first leg of the Ymer 80 expedition (Danielsson, Westerlund, 1983). They show little variation with depth, with the surface samples perhaps showing slightly lower concentrations. Most of the results from the second leg of Ymer 80 (Mart *et al.*, 1984) are somewhat lower. There appears to be a distinction in these data (Mart *et al.*, 1984) between the outflowing western part of Fram strait (lower concentrations) and the inflowing eastern part. The eastern stations overlap with the locations of first leg of Ymer and Fram. The nickel concentrations for these eastern stations also agree better with the Ymer (first leg) and Fram results. Cesar results are quite different. As was the case for cadmium, the surface concentrations are higher than at Ymer and Fram and a concentration maximum is seen at 100 m. The nickel concentration in this maximum is quite similar to that observed in the surface waters at Geosecs station 219 (Boyle *et al.*, 1981). In the deeper waters the nickel concentrations at Cesar would appear to be intermediate between those from Ymer (1st leg)/Fram and the western stations from Ymer (2nd leg).

The zinc profiles are shown in Figure 4. The zinc concentrations of the shallowest samples from each profile are very high and these have been excluded in the calculations of average concentrations. As would be expected, there is more scatter and poorer agreement among data from different laboratories for zinc than for the other metals. This is because contamination problems are generally more severe for zinc than for any of the other metals. The contamination problem necessarily makes conclusions about the zinc distributions more tentative than for the other metals. Nevertheless, similarities are seen between the profiles for zinc and cadmium. The most important feature is the zinc maximum at 100 m. This is seen in both the Lorex and Cesar data with a maximum concentration of ~ 6 nM in both cases although the feature is somewhat obscured by the scatter in the data. The concentrations at this maximum are considerably higher than would have been predicted on the basis of Bruland's (1980) Pacific Ocean zinc:silicate relationship but may reflect Bering Sea zinc concentrations.

The manganese results are illustrated in Figure 5. The manganese results from Fram (unfiltered samples) show decreasing concentrations from the surface down to mid-depth. This type of trend is seen almost universally for manganese. In the very deepest water three rather high concentrations were measured. These most likely result from higher levels of particulate matter in these bottom waters. Similarly high deep water iron concentrations were seen by Danielsson and Westerlund

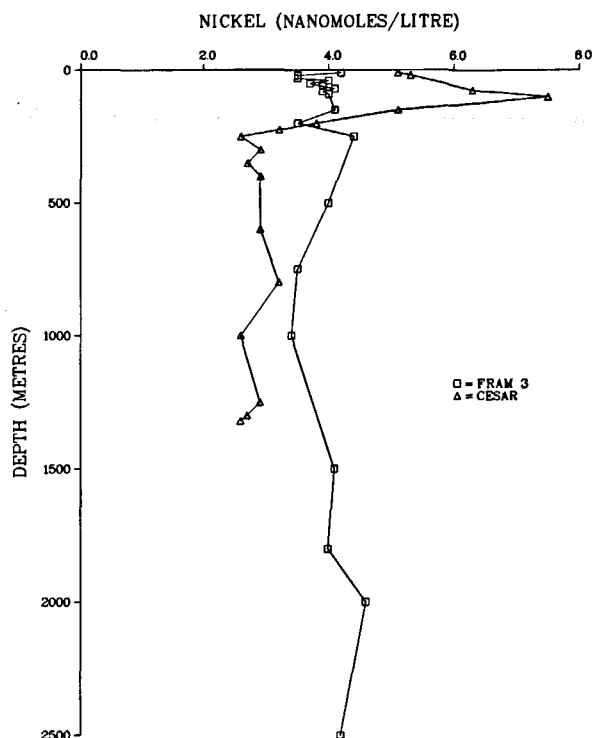


Figure 3
Nickel profiles for Fram 3 and Cesar.

(1983). At Cesar, concentrations were lower because the Cesar samples were filtered, but the same trend of decreasing concentrations with depth was observed. No near bottom increases were seen. The manganese concentrations at the depth of the Cesar nutrient maximum are low and quite similar to those observed in the surface waters at Geosecs station 219 (Klinkhammer, Bender, 1980).

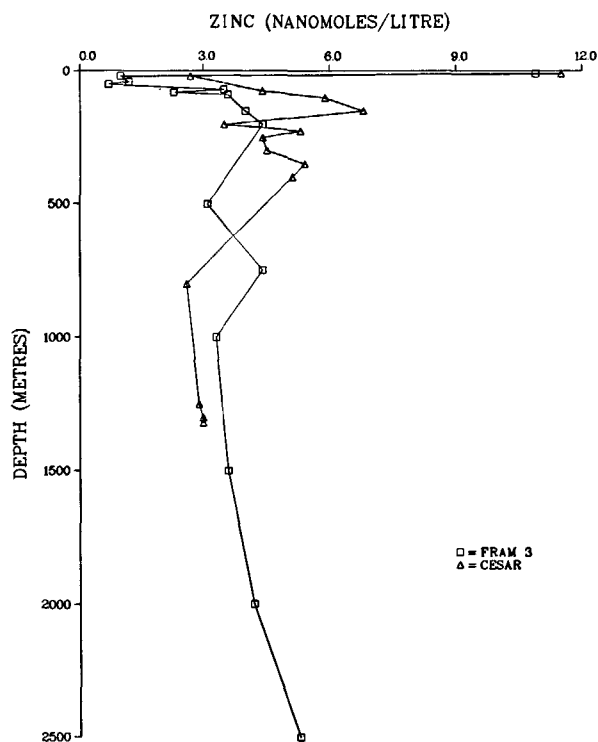


Figure 4
Zinc profiles for Fram 3 and Cesar.

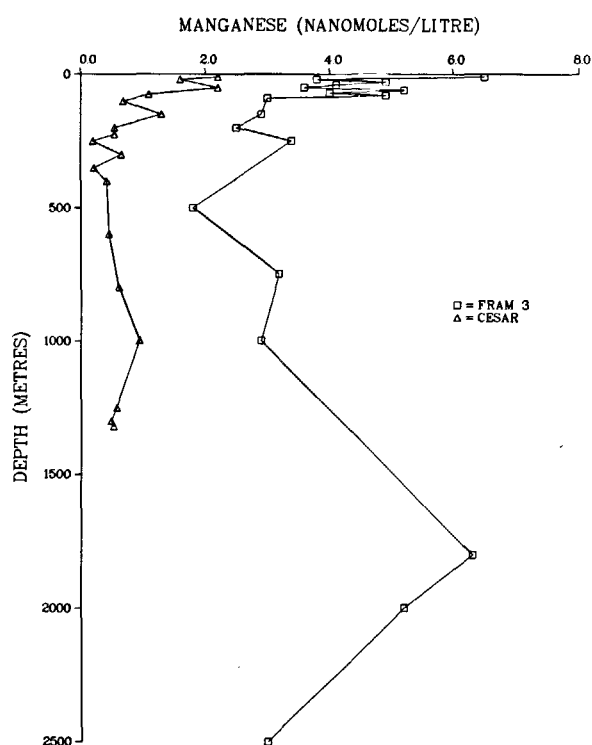


Figure 5
Manganese profiles for Fram 3 and Cesar.

DISCUSSION

In the most general terms, the metal concentrations in the Atlantic layer and the deep waters are uniform throughout the regions of the Arctic Ocean where measurements have been made. This consistency is seen over four expeditions to the Arctic with analyses conducted by four different laboratories. The concentrations in these layers reflect metal concentrations in the waters of the North Atlantic and Norwegian Sea that form the source for the deeper Arctic waters (Danielsson *et al.*, 1985).

In the surface waters, there is a clear distinction between the levels of Cd, Ni and Zn from Ymer and Fram and those from Lorex and Cesar. In all cases, the Ymer/Fram results, which predominantly reflect concentrations in the surface waters of the southern Eurasian basin, are lower. This observation is consistent with the fact that the surface water at Fram 3 is formed predominantly from cooled Atlantic water with relatively little dilution by freshwater runoff. The metal levels are similar to those in the Atlantic layer but slightly lower probably as a result of biological uptake. The surface waters (<70 m depth) of the large clockwise gyre in the Canadian basin (Lorex and Cesar) are influenced by meltwater and the large riverine input from the rivers of eastern Siberia, Alaska and Northern Canada. As a result, the salinity of this water is considerably lower and metal concentrations are elevated. The extensive shelf areas may also be contributing to the elevated metal concentrations since shelf sediments are known to be sources for at least some of the metals.

The other prominent feature of the Canadian basin profiles is the 100 m anomaly for Cd, Ni and perhaps Zn. The nutrient anomaly at this depth has long been known (Kinney *et al.*, 1970) and the coincident cad-

mium anomaly was first seen by Moore (1981). These were both attributed to the advection of Bering Sea winter water high in nutrients and metals into the Arctic. More recent work on nutrients and alkalinity has examined more closely the role that salinization of the halocline (see Aagaard *et al.*, 1981 and Melling, Lewis, 1982 for an explanation of this mechanism) and nutrient regeneration on the continental shelves may play in the formation of these anomalies (Moore *et al.*, 1983; Jones, Anderson, 1986). Jones and Anderson argue that the nutrient, especially nitrate, and carbonate concentrations at Cesar are inconsistent with a direct Bering Sea source and that nutrient concentrations are modified by processes occurring on the shelves. Lead-210 data from Cesar have also been explained in terms of interactions with the sediments (Moore, Smith, 1986).

The results presented here for Cd, Mn and Ni are consistent with the advection into the Canadian basin of Pacific Ocean surface water from the Bering Sea with its trace chemical composition altered only by *in situ* regeneration. Geosecs station 219 surface concentrations for these metals are all very similar to those found at 100 m in the Arctic (Boyle *et al.*, 1976; 1981; Klinkhammer, Bender, 1980). Surface cadmium concentration is 0.61 μM at Geosecs 219 and 0.59 and 0.62 nM at the Lorex and Cesar nutrient maxima. Manganese concentrations are 1.3 and 1.0 nM at Geosecs 219 and Cesar respectively, and nickel, 6.1 (Geosecs) and 6.3 nM (Cesar). Copper results from Lorex (Moore, 1981) do not show a maximum coincident with the nutrient maximum. This is consistent with a Bering Sea source since copper concentrations in the offshore high salinity surface waters of the Bering Sea are fairly low (<3 nM, Boyle *et al.*, 1977; Heggie, 1983).

Sediment sources or other interactions with the sediments have been invoked to explain several of the observed chemical profiles in the Canadian basin, particularly features associated with the nutrient maximum (Moore *et al.*, 1983; Moore, Smith, 1986). The two metals that might be expected to show the best evidence of releases from the sediments would be copper and manganese (Boyle *et al.*, 1981; Heggie, 1983; Yeats *et al.*, 1979). Elevated Cu concentrations are seen in the surface waters (Moore, 1981) and these may be partly related to release of Cu from the sediments but the high Cu concentrations do not seem to be associated with the nutrient maximum. Likewise, there is no indication of high Mn concentrations in association with the nutrient maximum. Lack of a sediment related signal for these metals does not rule out sediment sources for other chemicals because the redox conditions or types of sediments may be inappropriate for the reactions necessary to generate metal fluxes from the sediments, however, it does place some constraints on the sedimentary environment that could be producing any other diagenetic signals.

Danielsson and Westerlund (1983) observed a Cd vs P relationship for their Ymer data that showed a distinctly different Cd/P ratio and residual Cd concentration at P=0 than those observed in the Atlantic (Yeats,

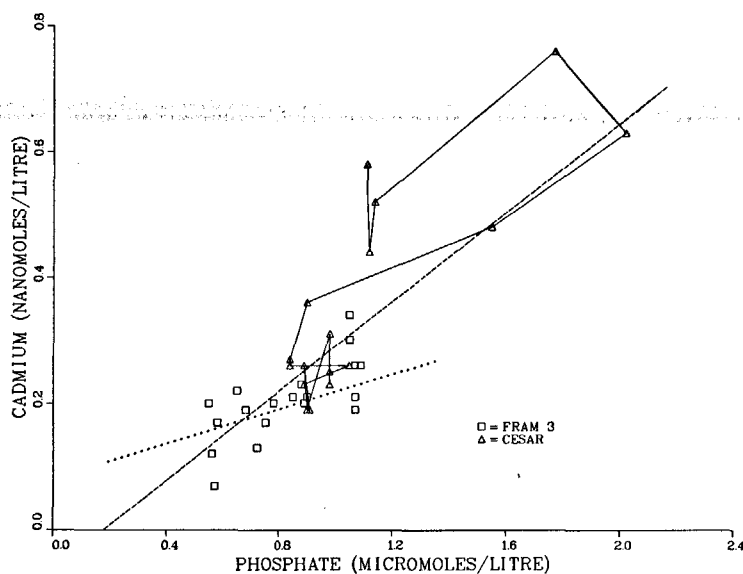


Figure 6
Plot of cadmium vs phosphate. The two straight lines depict the Cd:P relationships for the northeast Pacific (Bruland, 1980) (---) and the eastern Arctic (Danielsson, Westerlund, 1983) (...).

Campbell, 1983) or Pacific (Bruland, 1980) oceans. As can be seen from Figure 6, the results from Fram agree very well with the Ymer results. The surface samples from Cesar or Lorex (Moore, 1981), particularly those from the 100 m anomaly, do not follow the same relationship. They are much better described by the Pacific Ocean relationship described by Bruland (1980). The deeper Lorex/Cesar data, however, are indistinguishable from the deep Ymer/Fram data. The fact that the cadmium concentrations in the nutrient maximum follow the Cd:P relationship for the Pacific Ocean so closely is further evidence for the advection of surface water from the Bering Sea altered only by *in situ* regeneration processes.

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