Trace metals as oceanic tracers, their interaction and residence

M. I. Abdullah
Marine Chemistry Section
Biology Institute
University of Oslo
Blindern, Oslo 3
Norway

ABSTRACT

Although trace metals are highly reactive in the sea, many of the reactions involving these metals either take place at the sea water/fresh water boundary or are sufficiently slow causing these metals to behave in a quasi-conservative manner, and consequently they may be used as tracers. Evidence for this may be seen in the composition of the various oceanic water masses which can be readily explained by the well established concepts of material transport to the sea and oceanic circulation.

INTRODUCTION

While salinity and temperature have been the fundamental properties for the study of water mass structures in the oceans, it has often been necessary to identify more specifically the origin of these water masses. For this reason and when salinity and temperature cannot provide the specificity, other substances have been used. Of note here are the radionuclides, nutrient salts and some organic compounds. The minor elements and in particular the transition metals have received little attention, since, in addition to uncertainties associated with analytical difficulties, their geochemical and biochemical reactivity are considered to render them inappropriate as water mass tracers.

For an element or a compound to be an ideal tracer, it must exhibit a conservative behaviour in the sea, that is, it should not undergo any reaction, loss, degradation or fractionation. There are very few elements or compounds that satisfy these conditions. For this reason, the choice of chemical tracers may be dependent on the scale both in time and space and the resolution required. For example, over a short period of time and on a small regional basis, nutrient salts have been successfully used as tracers (Abdullah and Royle 1973).

The use of trace metals in water mass characterisation has attracted little attention in the past except on a local coastal scale. This is surprising since a great deal is known of their chemistry and behaviour in the sea. In recent years a great deal of the analytical difficulties have been eliminated, and many laboratories possess the necessary equipment and expertise in metal determination, making possible the application of trace metals in water mass studies. In this article the important features in the chemistry of trace metals, reactions and equilibria are highlighted with the view of examining the possibility of their use as tracers.

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In this context, two topics will be considered, namely input to the sea and processes (chemical, geochemical and biochemical interaction).

METAL SOURCES TO THE SEA

The main sources of metals are: a) rivers and runoff, b) the atmosphere, c) hydrothermal and geothermal activities and d) the sediments (fluxes associated with early diagenesis). Sources a) and b) will now be considered.

a) *River input and runoff.* By far the most significant material flux occurs through rivers and land runoff (Garrels and Mackenzie 1971). The trace metal content of river water shows a high degree of variability associated with the varied composition of the rocks constituting the catchment area of rivers (Livingston 1963; Durum and Haffty 1963; Martin and Meybeck 1979; Martin and Whitfield 1983). The existence of mineral deposits as well as discharges of industrial waste often produce 2 or 3 orders of magnitude difference in the concentration of some metals (e.g. Zn, Pb, Cd, Hg, Ni). Such differences, therefore, will impart significant compositional variations to sea water. The use of such variations for water mass studies depends on how stable these are with time.

Equilibria that are well poised under low ionic strength of river water, become unstable with increase in the ionic strength of the medium upon mixture with sea water. Such equilibria involve the stability of colloids, hydrolysis, adsorption/desorption reactions and precipitation reactions. Elements that are not involved in these equilibria generally show linear mixing relationship (concentration versus salinity) between the two end members, river and sea water, and their behaviour is regarded as concervative. Others will exhibit concavity or convexity in their mixing relationship depend-
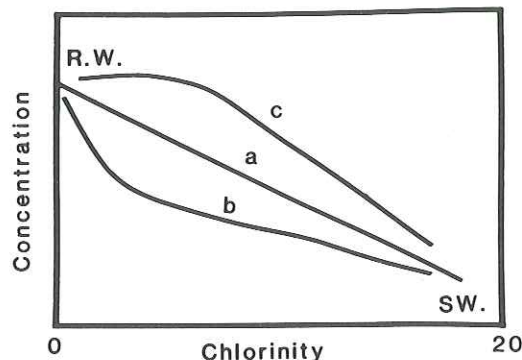

Fig. 1. Idealised mixing relationship between river water (RW) and sea water (SW). a: Conservative, b: loss of component, c: release of component.

ing on whether release or loss of an element is involved (Fig. 1).

The precipitation of colloidal iron in near-shore waters has been demonstrated by many workers (Aston and Chester 1973) and the effects this can have on the concentration of other metals through coprecipitation can be significant. The loss of metals such as manganese from solution clearly depends on the physico-chemical conditions affecting their oxidation state and hydrolysis. In addition, the presence of particles can dramatically affect the kinetics of these reactions as has been shown by Morris and Bale (1979) who have demonstrated that about 60 mg l^{-1} load of particles will cause the total loss of dissolved manganese within 6 days of incubation. Such load of particles is often encountered in estuarine and coastal waters.

The role of particles extends also to adsorption-desorption reactions, involving many of the trace metals. The equilibria in such reactions depend not only on the load but also on the nature of the particles, pH and ionic strength of the solution. For a given metal, e.g. Cu, and at a given pH, adsorption decreases with increase in the ionic strength of the medium (Bourg 1983).

Studies on estuarine mixing have shown that the greater change associated with

admixture of saline solution occurs at relatively low salinities (Morris et al. 1978) and that at a salinity of few parts per thousand, equilibria with respect to sea water will be almost established except perhaps those affecting clay minerals. At higher salinities some metals would, therefore, behave in a "conservative" manner. An example of such behaviour was described by Boyle et al. (1982) who found a linear relationship between Cu and salinity in the R. Amazon plume making it possible to identify the Amazon water. Similarly, the conservative behaviour of Zn, Ni, and Cu in near shore waters, in the absence of competing biological interactions, have been utilised (Abdullah and Royle 1973) to identify different sources of discharges in Liverpool Bay (Fig. 2). The dispersal of these discharges and their areal distribution were estimated. As the eddy diffusion coefficient was relatively large in this region, steady-state conditions were assumed to be established in a short period of time, e.g. 2-3 months, when these metals could be regarded as conservative.

Beyond the estuarine mixing zone, there is evidence that equilibrium between metals and particles is achieved fairly rapidly and that in the open sea, a number of metals could be regarded as conservative. Moore's (1981) observation in the central Arctic, suggests that the enriched Cd level in the surface layer could be accounted for by runoff, thus illustrating its conservative behaviour. The level of Cd in the surface layer of the oceans (Table 1) shows the effects of runoff. Here the NW and NE Atlantic surface layer contains higher level than that found in the Central and South Atlantic and South Pacific. Such differences, therefore, may be used to examine the coherence and mixing of the ocean surface waters.

b) *Atmospheric transport.* While mainly organic tracers such as PCBs and hydrocarbons are significantly carried to the ocean through atmospheric transport, only few metals are involved. Of note are lead and mercury. In the absence of other sources, the enrichment in the oceanic surface layer with these metals have been associated with this mode of transport and the extent of such enrichment is clearly dependent on the atmospheric flux. In this context, Schaule and Patterson (1981, 1983) concluded that the greater enrichment of Pb in the North Atlantic surface layer (170 p mol l^{-1}) than that of the Pacific (70 p mol l^{-1}) must be attributed to the greater flux of atmospheric Pb in the North Atlantic. Because of the nature and the wide spread of atmospheric transport, differences could only be identified on a regional basis and small differences could not be ascertained. Examples of the concentrations of some selected trace metals in the world ocean are given in Table 1.
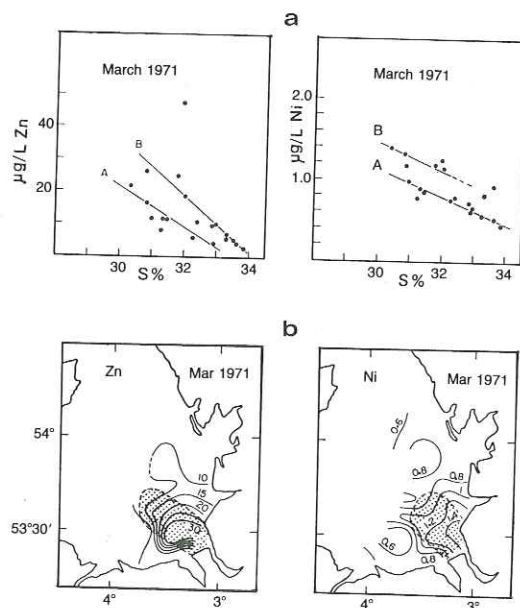

Fig. 2. a) The relationship between Zn and Ni concentrations and salinity for the two water masses A and B. b) The areal (surface layer) distribution of water masses A and B (shaded) in Liverpool Bay. (From Abdullah and Royle 1973).

TABLE 1

The concentration (μM) of selected trace metals in the world oceans.

	Ni	Cu	Zn	Cd	R
Atlantic Ocean					
NW Atlantic, 3 stations	3.3–5.7	1.8–3.7	0.7–8.6	0.21–0.4	(1)
	3.6–4.3	1.7–2.8	3.0–5.4	0.23–0.45	(1)
	2.4–4.8	1.4–3.3	1.2–7.6	0.03–0.60	(1)
North Atlantic	—	—	—	0.18–1.3	(9)
Surface Water	—	4.0	2.4	0.21	(6)
35°N, 32°W – 57°N, 11°W	3.40	1.28		0.040	(2)
7°S, 35°W – 35°N, 3°W	1.88	0.86		0.026	(2)
Indian Ocean					
0–100 m	5.1	3.5		0.013	(3)
100 m	9.4	3.8		0.057	(3)
Pacific Ocean					
0–100 m	3.9			0.023	(4)
100 m	10.4			0.082	(4)
Equatorial				0.034–0.082	(5)
South New Zealand				0.007–0.088	(5)
North Pacific,					
surface	2.5	0.5	0.34	0.002	(7)
below 500 m	11.0	2.0	9.0	1.1	(7)
Arctic Sea					
0–100 m		4.1–5.4	2.3–6.1	0.24–0.61	(8)
100 m		1.4–8.8	1.5–4.1	0.13–0.21	(8)

(1) Yeats and Campbell (1983), (2) Kremling (1985), (3) Danielsson (1980), (4) Boyle et al. (1976), (5) Raspor (1980), (6) Bruland and Franks (1983), (7) Bruland (1980), (8) Moore (1981), (9) Eaton (1976).

PROCESSES AFFECTING TRACE METALS IN SEA WATER

Enrichment of sea water with metals, and their level, can generally be attributed to the major sources of input. The actual profile and distribution of metals in the sea must eventually be determined by the state of equilibrium involving a number of reactions in sea water. These are either purely chemical: precipitation, oxidation/reduction, hydrolysis or geochemical, involving solid phases through adsorption/desorption, or biochemical involving bio-accumulation and release.

The existence of metals as dissolved species in sea water will depend on their behaviour at the prevailing Eh and pH conditions. A simple model based on the solubility of metal salts would produce entirely different metal levels in sea water than those observed in the present sea. Interaction with particles including metal precipitates (e.g. Fe, Mn) must be the key factor in controlling the metal levels. The extent of such interaction must, therefore, depend on both the structure and composition of the particles and the chemistry of the metals. Whitfield and Turner (1982) have suggested

that the partition coefficient, K_p (concentration in sea water / concentration in particles) of metals correlates with their hydrolysis ($*K_1$) or acid dissociation (K_1, K_2) constants in natural waters. The degree of geochemical reactivity of the elements was shown to be of the same order in sea water as in fresh water. Whitfield and Turner (1982) have demonstrated this by comparing metal content of deep sea clays and river suspended matter and found a high degree of correlation.

In addition to chemical reactivity, pH, ionic strength and the composition of particles play an important role in adsorption reactions. Bourg (1983) has shown that adsorption of Cd on SiO_2 at a given pH decreased with increased ionic strength of the solution while no such change was observed for Cu. Natural sediments from the Gironde Estuary and the Rhine river were also examined. The former showed greater adsorptive capacity for Cu, Zn and Cd than the latter at any given pH, reflecting the compositional differences in the sediments.

The kinetics of metal adsorption by clay minerals in the sea is not well known. However, the composition of particulate matter shows that for some metals (Mn, Fe, Th, Cu) there is an increase in the ratio of metal/Al with depth while for other, e.g. Sc, increase is slight with depth (Brewer et al. 1980). It is difficult to interpret these ratios since the particulates are heterogenous and variable in composition. Balistrieri et al. (1981) suggested that adsorption on the organic fraction and the subsequent release and re-adsorption may be an explanation. Re-adsorption, thus, would depend on both reactivity of the element and adsorptive capacity of the particles. The steeper depth profile of Ag than that of Cu in the eastern Pacific (Martin et al. 1983) may be accounted for by the difference in the adsorptivity of the two metals on marine particulates, especially the stronger affinity of Ag to organic particles.

Although marine sediments may be regarded as the ultimate sink for metals in the sea, remobilisation often occurs at the sediment/water boundary or within the sediment. The mineralisation of organic matter arriving at the sediment surface both liberate combined metals and alter the chemical regime there through consumption of oxygen and the production of reducing conditions. In such cases a number of well known metal scavenging agents (e.g. hydrated ferric oxides and manganese dioxide) may redissolve, thus liberating associated metals. Under such conditions the sediments may act as a source of metals to the overlying water (Abdullah and Egeberg 1984). Such a process is significant on small scales, e.g. in estuaries and fjords. The high content of Fe and Mn in bottom water of anoxic fjords is a characteristic feature (Agerup 1984; Schaanning 1983) — which can be utilised for tracing such water upon its upwelling. On oceanic scale, the importance of metal remobilisation from the sediments is not clear. However, Jones and Murray (1985) presented evidence of such mobilisation involving Mn from the continental slope in the Northeast Pacific off Washington, under suboxic conditions in the sediments. Such release gives the adjacent water masses characteristically high level of the element. Metal enrichment in the deep oceanic water (e.g. Mn), on the other hand, has been mainly attributed to injection of hydrothermal fluids (Klinkhammer 1980; Jones et al. 1981). In all these cases the total metal content acts as a useful index (Fig. 3) but only on a short time scale.

Biological interaction with metals through uptake and release by excretion or upon degradation of organic matter is now recognised as a mechanism for transport and redistribution in the sea. This process determines particularly the metal content in
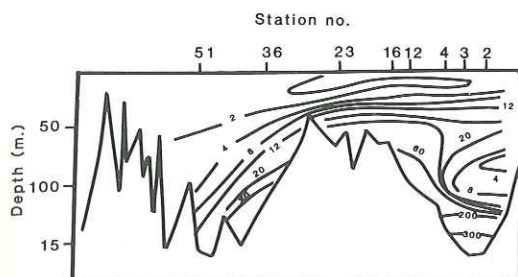
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Fig. 3. The distribution of Mn (μg l^{-1}) along a longitudinal section in the Inner Oslofjord in 1982. (From Agerup 1984).
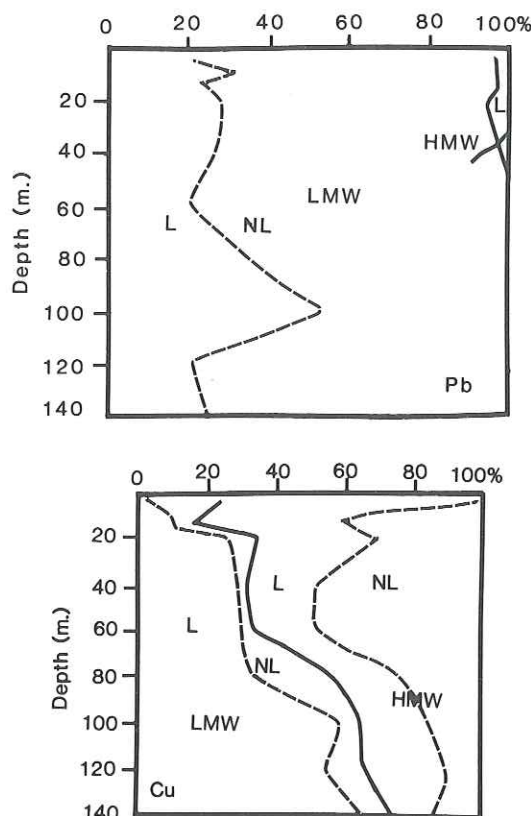
Fig. 4. The proportion (%) of total Cu and Pb present in separate fractions in sea water from the Inner Oslofjord. HMW: high molecular weight, LMW: low molecular weight fractions. L: labile, NL: non-labile. (From Hasle and Abdullah 1981).

the deep water of the sea and its profile therein. Recently and with improved methodology for metal analysis, profiles for some metals similar to those of nutrient salts have been determined, indicating the role of biological interactions (Boyle et al. 1976; Bruland 1980). Both excretion and degradation of biological material involve the initial production of soluble organic compounds such as amino acids and "humic"-like dissolved organic matter (DOM). The role of DOM in trace metal chemistry has been demonstrated by many workers (Duiker and Kramer 1977; Figura and Mc Duffie 1980; Mantoura et al. 1978). Metal-organic complex formation not only maintains metals in "solution" but is also significant in the equilibria for trace metals in sea water, particularly with respect to ion-exhange and adsorption-desorption reactions. Here, clearly, the type of association between metals and the organic molecule is highly relevant. Operationally, however, the associations may be divided into labile, and non-labile depending on the kinetics of the dissociation of the complex. Similarly, metals may be associated in complex formation with organic matter of different molecular weight or size. The presence of these complexes and their stability will depend on the presence of other competing agents such as clays or hydroxides and on the stability of organic matter.

Eventually, mineralisation of organic matter will liberate metals to the sea water.

In areas of high organic production, such as the Oslofjord, a significant part of the dissolved metal is organically bound and may be stable for considerable time. In such areas it is found that in the upper part of the water column, the bulk of the organic matter is possibly composed of the first degradation products and consequently, largely macro-molecular. These forms decrease with depth in favour of low molecular weight fractions. The partition of Cu, for example, reflects the distribution of organic matter in the sense that most of the

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Cu in the upper layer is associated with the high molecular weight fraction (HMW) and is labile (Fig. 4). This then decreases with depth, and at say 100 m the Cu is mainly associated with the low molecular weight fraction (LMW). Elements such as Pb, on the other hand, show a different partition (Fig. 4). Throughout the water column it is mainly associated with the LMW and is non-labile (Hasle and Abdullah 1981). Such differences may, in addition to the metal's chemical affinity and reactivity, depend on whether a metal is strongly accumulated by planktonic matter (e.g. Cu) or not accumulated (e.g. Pb).

INTERNAL CYCLING AND METAL CHARACTERISATION OF OCEANIC WATER MASSES

It is reasonable to assume that all the processes outlined above take place to a various extent in different parts of the oceanic water column. While adsorption-desorption reactions predominate at the freshwater/seawater boundary, they will also occur in open sea water involving metals liberated upon oxidative degradation of organic matter. However, the importance of each process will be seen in different parts of the water column. For example, biological removal will predominate in the euphotic layer, while release will take place mainly below it. Thus at any time it may be assumed that metals are in a steady state equilibrium with respect to these processes and within the general hydrographic regime. Upwelling, downwelling and advective diffusion are the main processes that will disturb such a steady state equilibrium. The stochastic model postulated by Spencer (1969), cited by Brewer (1975), illustrates the general aspects of the equilibrium where interaction between particulate matter (including organics) and dissolved metal acts to maintain equilibrium concentration. The kinetics of these reac-
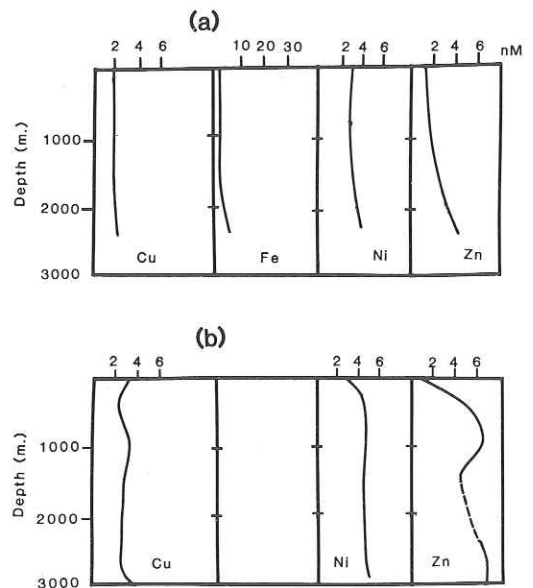

Fig. 5a and b. The profiles of Cu, Fe, Ni, and Zn in a) the Arctic Basin (after Danielsson 1983) and b) in the North Atlantic. (After Yeats and Campbell 1983).

tions vary depending on the process and the element involved. An example is the nickel distribution in the Gulf Stream and its mixing with Atlantic surface water. Here, Spencer and Brewer (1969) found that the Gulf Stream water retained its concentration of Ni and that its behaviour is quasi-conservative suggesting that removal processes are very slow.

Combining the runoff and atmospheric influence on the surface layer composition and the biological interaction with oceanic circulation, it is possible to characterise oceanic water masses in terms of their trace metal content. The effects of biological cycling together with the deep water circulation in the Atlantic and Pacific should produce differences in the metal profiles (increase with depth) similar to those observed for NO_3 and PO_4. Thus in the Arctic Basin and the North Atlantic we would expect a weakly developed profile with depth. The observation made by Danielsson and Westerlund (1983) shows that Cu, Ni, Zn

and Fe, all biologically important metals, occur at very low concentrations throughout the water column of the Arctic Basin (Fig. 5a). Little or no variations were reported for Cu, Ni or Zn, while Fe exhibited a slight increase in the surface layer.

The observation of Yeats and Campbell (1983) in the North Atlantic (Fig. 5b), however, shows higher values for Ni, Cu and Zn in the deep water (4-5, 2-3 and 4-7 nM respectively) than those observed in the Arctic Basin suggesting some accumulation in the deeper water. The data of Yeats and Campbell also show the surface layer to be biologically depleted of these metals bringing about a better developed biological profile.

The differences in the trace metal distribution in the oceans produced by the various processes is best illustrated by comparing their profiles in the North Atlantic with those in the North Pacific. It is generally recognised that for many dissolved species, the biological transport down the water column coupled with oceanic circulation leads to a material accumulation in the North Pacific. Such accumulation has been well documented for the nutrient salts and the near-depletion of dissolved O_2. Over recent years, improved sampling and analytical methodology for some trace metals have provided reliable data for these metals to be examined in this context.

Comparison of North Atlantic and North Pacific trace metal profiles has recently been made by Bruland and Franks (1983) based on published data from Bruland (1980), Landing and Bruland (1980) and Schaule and Patterson (1983) and is illustrated in Figure 5c. For Ni, Zn and Cd (metals which are strongly associated with the biota) the deep water concentrations in the North Pacific are about 3-4 times greater than those in the North Atlantic. Although other metals, such as Mn and Cu, are similarly associated with the biota but exhibit greater geochemical reactivity, their
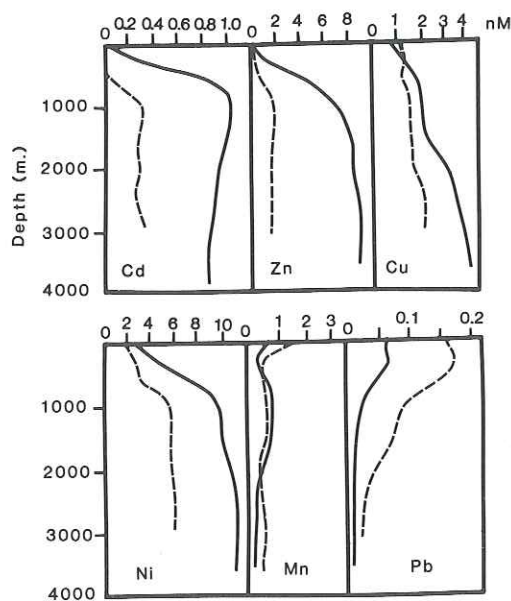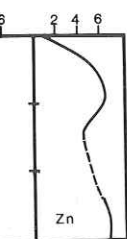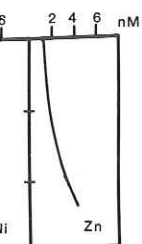

Fig. 5c. Comparison between metal profiles in the North Atlantic (– – –) and the North Pacific (——). (After Bruland and Franks 1983).

profiles are not greatly dissimilar. Only Cu shows significantly higher level in the Pacific deep water than in the Atlantic deep water. Other metals such as Pb which are transported mainly by atmospheric processes and runoff, and exist mainly as recent pollutants playing a minor biological role, are found enriched mainly in the upper part of the water column. Here, the North Atlantic which receives greater amounts of Pb, shows the higher concentration, about 3 times that of the North Pacific. Advection and turbulent diffusion (and perhaps to a lesser extent in the case of Pb, geochemical processes of uptake and release) transport Pb to the deeper water. The effects of such transports are, therefore, observed only down to about 2000 m below which only very low background levels of Pb are observed.

At present it is difficult to ascertain the constancy of these profiles on a regional basis due to the scarcity of data. Patchiness in the surface layer distribution and the ef-

fect of e.g. hydrothermal activity in certain parts of the ocean floor may greatly modify these profiles. The distinctive and specific metal distribution should make it possible to characterise deep sea water masses at least on a qualitative basis. Of particular interest are the physical processes in the upper 1000 m of the water column which may be examined using, in addition to organic compounds, elements such as Pb and Hg.

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