Translated from *Uspekhi Khimii*, **55**, 1023-1052 (1986) U.D.C. 551.464.38(260)

The Forms of Trace Elements in the Abiotic Phases of Natural Aqueous Media

A.K.Prokof'ev

The literature data on the phase, physicochemical, and chemical properties of trace elements (microelements) in the abiotic phases of natural aqueous media—the atmosphere, the surface microlayer of water, natural waters, suspended and colloidal particles, bottom deposits, and pore waters, as well as the mechanisms of the interconversions of these forms are surveyed and critically examined. The ways in which trace elements are absorbed and removed via the interfaces of these phases and on mixing in the estuary as well as the causes of such sorption and removal are considered. It is shown that the form of the trace elements in the phases of all types of natural waters (in oceans, seas, rivers, estuaries, lakes, and bogs) plays a decisive role in their transport, biological availability, and biogeochemical cycles.
The bibliography includes 368 references.

CONTENTS

I. Introduction 562
II. The atmosphere 563
III. The surface microlayer on water 564
IV. Natural waters 564
V. Colloidal and suspended particles 568
VI. Estuarine mixing 570
VII. Bottom deposits and pore waters 571

I. INTRODUCTION

In many industrially developed countries the present degree of pollution of individual internal water basins and regions of coastal sea waters by chemicals of anthropogenic origin exceeds the ecologically safe level. Together with organochlorine compounds and petroleum, the toxic elements Hg, Pb, Cd, As, Cu, Se, as well as others whose concentration in natural waters (NW) is less than 1 mg kg^{-1} (1 p.p.m.) constitute a special danger. They are referred to as trace elements (TE) and they do not include biogenic and radioactive elements or dissolved gases.

The determination of such extremely low TE concentrations in natural aqueous media constitutes an extremely difficult analytical problem. The situation is greatly complicated by the fact that at any stage of the analysis, especially in the removal and preliminary treatment of samples, it is very easy to contaminate the latter from the sampler, air, reagents, the vessels used, and other sources. This is particularly important for ocean waters, in which the concentration of many TE is lower by several orders of magnitude than in surface waters and can amount to 1 ng kg^{-1} (p.p.t.). As the above causes of the contamination of samples in analysis have been eliminated and the sensitivity and selectivity of the analytical methods for the determination of TE have improved, their measured content in NW, including ocean waters, has steadily decreased during the last decade, by orders of magnitude despite the constantly increasing anthropogenic injection of TE into NW. However, this trend has been sharply retarded in recent years and the concentrations of many TE established at present, even in ocean waters,[1,2] may be regarded as sufficiently reliable. They will be quoted below in the appropriate sections. However, the main bulk of the data concerning the content of the TE in sea waters, published up to 1975,[1] and in river waters, probably up to 1973, must be rejected.

However, the overall content of TE in aqueous media still does not reflect the true degree of pollution of the latter. Studies in various countries of the causes of numerous instances of the poisoning of hydrobionts by TE made it possible many years ago to reach the important conclusion that the biological accessibility and toxicity of TE depends very greatly on the form in which they exist. The data accumulated at the present time also permit the assertion that the forms in which TE exist plays a decisive role in their transport in the biogeochemical cycle. The knowledge of the form in which TE exist in aqueous media has therefore assumed first class importance.

Two main approaches are used to study the forms in which TE exist in NW. The first is theoretical and involves the calculation of the equilibrium concentrations of all the dissolved forms with the aid of mathematical models based on the employment of the experimental concentrations of TE and ligands as well as the published stability constants of the TE–ligand bonds. Chemical modelling embraces at the present time all possible competing equilibria; computer programs are employed for thermodynamic calculations. The accuracy of the computer modelling is however greatly reduced as a consequence of the uncertainty of the published stability constant and activity coefficient data. Furthermore, many parameters influencing the forms in which TE exist are not as a rule included in the calculation in view of the lack for the majority of them of qualitative and quantitative data concerning the pH, the redox potential, the nature of the vast majority of organic ligands, colloidal particles and the adsorption on them, the interfacial precipitation reactions, dissolution and sorption, biological and physical processes, etc. These factors as well as the lack of information about the non-equilibrium conditions which exist in many NW yield calculated results which are extremely doubtful. The advances in the field of chemical modelling have been described elsewhere.[3-6]

Another approach to the study of the forms of TE is analytical. All the experimental forms of TE in the abiotic phases of natural aqueous media can be usefully divided into three large groups—the phase, physicochemical, and chemical forms. The particular phase form to which the TE belongs is determined by the principal phases of aqueous media in which the TE is present—the natural atmospheric layer, the surface microlayer (SML) of water, NW, suspended and colloidal particles, deposits in aqueous media, and pore waters. A classification based on the physicochemical forms depends on the presence of the TE in specific fractions of aqueous media (for example in the dissolved organic fraction, the suspended inorganic fraction, and the sorbed fraction), which are subdivided either in terms of their size (established, for example, by ultrafiltration and gel filtration) or in terms of the lability of the fraction in relation to the analytical technique employed (for example, ion exchange or inversion voltamperometry are used for this purpose). The chemical forms can exist in aqueous media as compounds of TE in various oxidation states [for example inorganic arsenic(III) and arsenic(V)], as organoelemental compounds (for example, MeHgCl and Bu_2SnMe_2), or as complexes (for example, vitamin B_{12}). In this classification the chemical forms of TE are frequently their physicochemical forms; the overall amount of TE in these forms yields the overall content of TE in each phase of natural aqueous media.

The distribution of TE and their forms in the phases of aqueous media enumerated above takes place via very complex pathways as a result of various chemical, physicochemical, physical, and biological processes, the mechanisms of which are still little understood. The available chemical data and phenomenological models do not permit the prediction of the distribution of TE, let alone their forms, between different phases of aqueous media, which constitute extremely complex systems usually possessing variable qualitative and quantitative compositions.

The analytical determination of the forms of TE in NW cannot be regarded as a problem which has been solved, firstly, owing to their extremely low concentrations and, secondly, owing to their sensitivity to the salt composition, pH, the content of dissolved organic and high-molecular-weight compounds, colloidal and suspended particles, and other conditions which depend both on the type of the NW and on the time of year. It is important to note that the equilibrium concentrations of different forms of TE in NW inevitably change when samples are taken, as a consequence of their contact with atmospheric oxygen and the walls of the sampler and changes in temperature and pressure, and also in the course of their separation (isolation) and analysis. These changes are indefinite, but it is essential to minimize them in all cases. A number of reviews have been published on the methods for the determination of the physicochemical[3,7–14] and chemical[7] forms of TE in NW.

The aim of the present review is to examine the phase, physicochemical, and chemical forms of TE in the abiotic phases of natural aqueous media—the atmosphere, the SML, NW, suspended and colloidal particles, deposits in aqueous media, and pore waters, and also the mechanism of their interconversions. Individual aspects of this question were discussed earlier in relation to TE,[15] Hg, Cd, and Zn,[16] Cd in sea water,[17] organoelemental compounds,[18,19] and TE in ocean waters.[20] The types and causes of the absorption removal of different forms of TE through the interfaces of the above phases and in estuarine mixing are also examined.

In view of the existence of the above problems in the analytical determination of TE and their forms in aqueous media, we shall consider here, with rare exceptions, only data published during the last 5–7 years. Owing to the limited size of the article, they will be only briefly described and many publications concerned with the topic under discussion will not be mentioned. Preference is given to the latest, fundamental information and also review articles.

II. THE ATMOSPHERE

The substances present in the atmosphere in the liquid (water), solid (aerosols), and gaseous states exist in variable concentrations. Among them impurities of natural origin include particles of sea salts, dust from active volcanoes and continental erosion, etc. while anthropogenic impurities comprise different types of smoke and gases ejected by industrial undertakings, automobile transport, etc. The chemical composition of aerosols and atmospheric deposits has assumed great importance both for the investigation of the pollution of the environment on a global scale and for the determination of their role in the establishment of the chemical composition of NW.

It has been shown that Hg, Pb, Cd, Se, Sb, and other TE are transported in the atmosphere over long distances above the oceans.[21] The content of these TE exceeds by 2–3 orders of magnitude their average concentration in the Earth's core. This applies, for example, to the aeolian suspension over the pelagic regions of the Atlantic Ocean,[22] but the latter has, however, a different origin.[23]

In the marine aerosols, whose content varies in the range 0.003–30 μg m^{-3},[24] many TE have been determined.[21–24] For example, the concentrations of Cr and Se over the Atlantic Ocean are 0.54 and 0.033 mg m^{-3} [24] and those of Pb are 0.98 and 0.15 mg m^{-3} in the southern and northern hemispheres,[25] whereas over the Pacific Ocean the concentrations of these TE are respectively 0.73, 0.028,[24] and 0.2 mg m^{-3}.[26] It is noteworthy that the TE in natural marine aerosols exist preferentially in the water-soluble, exchangeable, and weakly bound forms.[24]

The content of the TE and their forms in rain water and in the gas phase has been studied to a lesser extent than in aerosols. The following amounts of TE have been observed in rain water (ng $litre^{-1}$): Hg 2 (open ocean),[27] Cd 320 (Lake Michigan),[28] Se(IV) 52.4 and Se(VI) < 5 (California),[29] As(III) < 2, As(V) 13.7, $MeAsO(OH)_2$ < 2 and $Me_2AsO(OH)$ 12 (California),[30] As(III) 214 and As(V) 4850 (Belgium),[31] Ge(IV) 0.5–0.7, Me_2Ge(IV) 1.0–5.9, and Me_3Ge(IV) 0.2–1.0 (Florida),[32] Sn(IV) 11, MeSn(IV) 5.9, Me_2Sn(IV) 7.4, and Me_3Sn(IV) 0.22 (Florida),[33] Me_nEt_mPb(IV), (n, m = 0–3) < 2–68 (Belgium),[34] Hg (inorganic) and Hg (organic) 12.2 and 0.8 respectively (Japan),[35] and Pb (inorganic) 133 × 10^3 and 280 × 10^3 [Antwerp, Belgium, suburbs and city centre respectively (Translator)].[34]

The fraction of mercury in the gaseous form corresponds to more than 99% of its entire content in the atmospheric forms in the natural atmosphere over the sea.[27] In the northern and southern hemispheres its concentrations in the pure atmosphere over the sea are respectively ~1.5 and ~1.0 ng m^{-3},[27,36] ~10% being present in the form of Me_2Hg.[36] About 50% of the mercury in the coastal sea atmosphere may be present in the organic form.[27] Data concerning the formation and fate of volatile molecular forms of TE have been surveyed.[37]

There is a constant reciprocal transfer of TE through the ocean–atmosphere interface, which are thus involved in the establishment of the chemical composition of both phases. The direction and rate of transfer are determined by the forms of the TE. The estimates of the fluxes for different TE and different regions of the world ocean can

differ markedly. Rains, which carry TE in a water soluble form, apparently play the greatest role in the atmospheric transport of TE to the ocean. It has been suggested[38] that, up to a depth of 100 m in the North Atlantic waters, 100% of Pb, 50% of Zn, Cu, and Mn, and up to 25% of Cd, Cr, and Al and other TE are of atmospheric origin. This has been demonstrated for Mn[39] and has been postulated for Se and Bi.[40] The atmospheric input of Pb has been studied in particularly great detail.[25,26,41,42] For example, it has been calculated that 24% of the lead entering the atmosphere annually is deposited on the ocean surface of the North Atlantic region.[25]

However, the exact sources of the TE brought through the atmosphere remain obscure. In certain regions of the world ocean Pb, Ni, Cu, and Zn are probably to a large extent of anthropogenic origin. They are formed, for example, by combustion of mineral fuels.[38,43] However, according to Jaworowski et al.,[44] the natural input of Pb, Hg, and Cd, for example, with atmospheric dust and products of volcanic eruptions, is of decisive importance.

The transfer of TE from the surface of the ocean to the atmosphere takes place as a result of wind action; TE are contained in the air bubbles bursting on the surface of the ocean and in the vapour. It has been observed that Cu, As, Hg, Pb, and other elements are mainly concentrated in the submicron fraction of sea aerosols,[23] in the establishment of the chemical composition of which the SML plays a major role, the latter being usually greatly enriched in TE compared with the bulk of the sea water (see Section III).

It has been suggested that considerable amounts of certain TE, particularly those forming gaseous methyl derivatives in the marine medium (Hg, As, Pb, etc.), pass from the surface of sea water to the atmosphere, since otherwise it would be impossible to balance their global cycles.[23,24] This can be regarded as proved for mercury.[27]

III. THE SURFACE MICROLAYER ON WATER

Studies in recent years have demonstrated that extremely important chemical and biological processes occur on the surfaces or at the interfaces of different NW phases. The latter include the interface between the ocean and the atmosphere—the SML, which is the site where many substances of natural and anthropogenic origin are concentrated (TE, petroleum and chlorinated hydrocarbons, detergents, etc.) as well as the habitat of a varied and abundant flora and fauna (neuston) with a much higher biological activity than in the lower water layers. The marine SML with its enormous size plays an especially important role. A series of reviews on chemistry and biology have been devoted to it.[45,46]

The physical stability of the SML is ensured by surface tension forces and by the presence of organic films. At the same time it is a climatically unstable medium subjected to much greater oscillations in temperature and salinity (S) than the subsurface water layer. In order to explain the available facts, a model has been proposed,[45] according to which the upper layer of the marine SML consists of a unimolecular lipid film 10–20 Å thick, below which there is a polysaccharide protein layer 100–300 Å thick and a layer, closely linked to it, of abiotic suspended matter of bacterioneuston, yeast, and mould (to a depth of ~1 μm). In marshes (saline bogs near the sea) two types of SML have been observed.[47] The commonest of these is opaque and is enriched in organic matter, while the second type encountered much more rarely, has a bluish colour and is enriched in iron.

Various SML serve simultaneously as sources and traps for substances in the atmosphere and in bulk water. The methods whereby TE and their forms are transferred in the ocean–atmosphere system have been described in Section II. They pass from the bulk of the water to the SML as a result of upwelling, convection, diffusion, and bubble flotation.

In the SML of all types of NW the concentrations of TE (Pb, Cu, Cd, etc.) and their forms are usually much higher than in the subsurface water layers. This has been demonstrated for lake,[48] river,[49] marsh,[50] and sea[43,51] waters. The above difference is especially large for the bound dissolved[49] and suspended[48] forms of TE. Their concentrations can differ by an order of magnitude and more [differences in concentrations reaching 4 orders of magnitude have been observed for $Bu_3Sn(IV)$, $Bu_2Sn(IV)$, and the total Sn in various NW of Canada[52]], which reflects a much higher content of suspended materials and of dissolved organic material in the SML compared with the bulk water. Although the forms of TE in the SML and their exchange with the bulk water and with the atmosphere are controlled by a series of processes which are not yet fully understood, it appears likely that the most important of these are surface adsorption on the suspension and complex formation involving the dissolved organic substance. The influence of a surface-active dissolved or colloidal organic substance on the chemical form and transport of Pb, Cu, and Hg through the marine SML has been discussed.[53] A decrease of the Fe and Mn contents in the SML as a consequence of the precipitation of the mineral particles carrying them[43] as well as the lack of enrichment by basic ions (K, Mg, Ca, Cl, and Br) have been observed.[51]

It is essential to note that many fundamental questions associated with the SML, including the entry, redistribution, and fate of TE and their forms have been clearly inadequately investigated. For example, the relative contribution of aerosols and bubble flotation to the enrichment of the marine SML by suspended TE remains obscure. According to some data,[43] they are approximately the same, while according to others, flotation predominates.[54] Furthermore, the lack of generally adopted samplers and methods for taking SML samples whose depths may differ by several orders of magnitude in the work of different investigators[45] makes it very difficult and sometimes even impossible to compare the experimental results.

IV. NATURAL WATERS

1. The Overall Content and Distribution of TE

As already noted above, the major advances in analytical chemistry during the last ten years and the elimination of contamination at all the stages of the analysis[2,55,56] made it possible to demonstrate that the concentration of the majority of TE in unpolluted ocean waters are in fact lower by 1–3 orders of magnitude than had been believed previously.[1,2]

The present data about the concentrations of all the elements in the Periodic System in open ocean waters have been compiled in two publications.[1,57] The first indicates for each element the proportions of inorganic forms in oxidised sea water calculated as described by Stumm and Morgan[4] and Turner et al.,[5] the range and average values of the concentrations, and the type of distribution and the the second gives the concentrations in the surface and deep (~1000 m) waters and predicts the average concentrations, the type of distribution, and the relation to the chlorine content. Table 1 lists the concentrations and types of pollution of the most important TE.[1]

It has been suggested that the vertical TE profiles be subdivided into 7 main types depending on the characteristics of the processes controlling them:[1] (1) the conservative type, which corresponds to the case where the concentration of the TE is independent of the salinity as a consequence of their low reactivity in sea water (this has been observed, for example, for Pb, Cs, and MoO_4^{2-}); (2) the biogenic type, in which the surface layers are depleted and the deep layers are enriched in trace elements as a result of their involvement in the biogeochemical cycle: the TE are removed from the surface layers of water by the plankton and the biological suspended particles formed, which descend to deeper regions, where the TE are regenerated via their oxidation or transition to a soluble state (for example, Cd, Zn, Se, and Ni); (3) surface enrichment and depletion in deeper regions when TE enter the upper layers of water (for example, from the atmosphere and rivers) and are then rapidly and constantly removed from the water (for example, Pb and Mn); (4) the minimum TE concentrations occur at an intermediate depth when TE fall on the surface of the ocean and are regenerated near its bottom, or are scavenged (adsorption on submerging particles) during passage through the bulk of the water (for example, Al and Cu); (5) the maximum TE concentration occurs at an intermediate depth due to hydrothermal activity (for example, Mn); (6) the minimum or maximum TE concentration occurs at an intermediate depth within incompletely oxidised layers associated with the occurrence of reductive processes in the bulk of the water or deposits on the adjoining continental slope [for example, Mn(II), Fe(II), and Cr(III)]; (7) the maximum or minimum TE concentration occurs in oxygen-free waters, established as a result of the interconversion of the SO_4^{2-}–H_2S air [for example, Mn(II), Fe(II), and Cr(III)].

Table 1. The concentrations and type of distribution of TE in ocean water.[1]

Element	Concentration, nmol kg^{-1}, for S = 35%*		Type of distribution
	range	mean	
Ag**	(0.5—35)	(25)	biogenic
Cd	0.001—1.1	0.7	»
Cr	2—5	4	»
Ni	2—12	8	»
Zn	0.05—9	6	»
Ge**	≤7—115	70	»
As	15—25	23	»
Se	0.5—2.3	1.7	»
Be**	4- 30	20	biogenic and scavenging
Cu	0,5—6	4	ditto
Al	(5—40)	(20)	minimum at intermediate depth
V	20—35	30	weak surface depletion
Mn	0.2—3	0.5	depletion in deep regions
Fe	0.1—2,5	1	depletion on the surface and in deep regions
Co	(0.01—0.1)	(0.02)	ditto
Pb**	5—175	10	high content in surface waters, depletion in deep regions
Sn**	(1—12)	(~4)	high content in surface waters
Sb	(1.2)	—	not established
Ti	(<20)	—	ditto
Au**	(25)	—	»
Hg**	(2—10)	(5)	»

*The round brackets show that the data are unreliable.
**The concentrations are given in pmol kg^{-1}.

In addition to the data quoted by Bruland,[1] vertical profiles have also been described for Ni, Cu, and Cd,[58,59] Zn,[58] Co,[60] Ag,[61] Fe,[62] Pb,[42] Hg,[63] Cr,[64,65] Mn,[66] V,[67] and the lanthanides.[68]

It is essential to note that concentrations of TE differ markedly in different oceans[2,55,69-71] as a consequence of the differences between the hydrographic parameters, biological productivity, and atmospheric input. The data for the same ocean obtained by different investigators[2] also show discrepancies due to the lack of a single methodological approach to the determination of TE. This has been confirmed by the comparison of different samplers[2,72] and analytical methods[73] and also by intercalibrations.[74]

The concentrations of TE in epicontinental seas and coastal waters are usually higher than in the open regions of the oceans (Table 2). We may also note data for the content of Hg (ng litre^{-1}) in the Sea of Japan (4.8[80] and 16.7[81]), the Sea of Japan [near the middle part of the mainland of Japan] (6.3 and 12.4),[81] the Bering Sea (5.8), the East and South China Seas (5.2),[80] and in the coastal waters of the USA (0.2–1.0[82] and 12.7[83]) and Japan (2.9—12.5),[84] and the content of Cr in the Sea of Japan (~0.45 μg litre^{-1})[85] and of Co in the San Francisco Bay (0.05—1.2 μg litre^{-1}).[60] A comparative study of the distribution of TE in oceans and coastal waters has been carried out.[71]

Table 2. The concentrations of TE in epicontinental seas and coastal waters (μg litre^{-1}).

Region	Cd	Cu	Mn	Ni	Pb	Zn	Refs.
Baltic Sea	0.027	0.661	0.341	0.810	0.016*	0.922	[75]
North Sea	0.033	0.925	—	—	0.148	—	[71]
Mediterranean Sea	0.008	0.090	—	—	0,035	—	[76]
Red Sea	0.005	0.090	—	—	0.013	—	[71]
Sargasso Sea	0.0002	0.08	0.13	0.12	—	0.004	[70]
Gulf Stream	0.017	0.16	—	0.23	—	—	[69]
Shelf waters of the USA	0.022	0.25	1.15	0.33	—	0.16	[70]
Bermuda platform	0.047	0.2	0.19	0.14	0.15	0.3	[77]
Gulf of Mexico	0.022	0.57	—	0.53	—	—	[78]

*Taken from Danielsson and Westerlund.[79]

Table 3. Concentrations of dissolved TE in rivers (μg litre^{-1}).

River	Fe	Mn	Cr	Zn	Ni	Cu	Cd	Refs.
St. Laurence	55	6.3	—	8.6	1.5	2.5	0.11	[86]
Mississippi	10	10	0.3	—	1	2	0.1	[87]
Amazon	2.0	19	2.0	—	0.27	1.8	—	[88]
Yukon	50	20	2.3	—	0.43	2.0	—	[88]
Hudson	32	1.5	—	4.6	1.9	3.2	0.20	[89]

The contents of dissolved TE in certain rivers are listed in Table 3. It is important to note that the majority of the TE are bound to a suspension (see Section V). In tropical rivers during the monsoon period, the concentrations of TE can decrease by a factor of several tens.[90] The average content of Hg is ~20 ng litre^{-1} in ten rivers of the USA,[83] 4.3–21.1 ng litre^{-1} in the surface waters of Japan,[35,91] 9.8 ng litre^{-1} in the River Thames,[92] and 6.6 ng litre^{-1} in the Ottawa River and 26.2 ng litre^{-1} in the Suimon River.[93]

2. The Physicochemical Forms of TE

Dissolved TE can be present in NW as part of the composition of the various physicochemical forms differing in their dimensions (Table 4). Several general schemes for the determination of these forms of TE have been proposed,[7,10] differing in the analytical methods employed and also in the procedures used for separation and decomposition.

Table 4. The possible physicochemical forms of TE in NW and their dimensions.[10]

From	Example	Approximate size, μm
Suspended	—	>0.45*
Simple hydrated ions of elements	Cd (II) $(H_2O)_6$	0.0008
Simple inorganic complexes	Pb $(H_2O)_4Cl_2$	0.001
Simple organic complexes	Cu glycinate	0.001—0.002
Stable inorganic compounds	PbS, $ZnCO_3$	0.001—0.002
Stable organic complexes	Cu fulvate	0.002—0.004
TE adsorbed on inorganic colloids	Cu (II) — Fe_2O_3; Pb (II) — MnO_2	0.01—0.50
TE adsorbed on organic colloids	Cu(II)-humic acid	0.01—0.50
TE adsorbed on mixed organic and inorganic colloids	Cu(II)-humic acid/Fe_2O_3	0.01—0.50

*It is retained on a filter with a pore size of 0.45 μm.

It must be emphasised that the dissolved organic matter, the main bulk of which (up to 80%) consists of highly oxidised biologically stable high-molecular-weight compounds, resembling the humic substances (HS) isolated from soil, play the main role in the distribution of the dissolved physicochemical forms. The rest of the organic matter consists of a mixture of polypeptides, polysaccharides, aminoacids, aliphatic acids, hydrocarbons, vitamins, and other compounds whose extremely low concentrations (usually less than 10^{-6} M) create serious analytical difficulties in their identification. The role of organic matter in river[94] and sea[95,96] waters has been examined in detail.

The exact structure of aqueous HS is unknown. They are high-molecular-weight polyelectrolytes of variable composition.[97,98] On the basis of chemical and spectroscopic data, it is believed that[98] marine fulvoacids and humic acids (HA) are structurally very similar, differing mainly by the absence of aromatic character in the former, and consist of cross-linked auto-oxidised polyunsaturated aliphatic acids.

The mechanism of the chemical binding of TE ions by HS is unknown, but it is believed that this interaction takes place via the formation of complex bonds of different types as a result of ion exchange, surface adsorption, and chelation.[99–101] The role of the HS is significant in the formation of complexes by TE, especially Hg, in surface waters,[102,103] but is much smaller in ocean waters (for example, for Cd, Pb, and Zn[104]), which can be accounted for by the different concentrations of the HS in these waters.

The specific organic forms of the TE in NW, with the exception of the vitamin B_{12}, chlorophylls, and a series of chemical forms, cannot currently be determined due to their extremely low concentrations. For this reason one either finds the overall content of the organic forms of TE or one analyses fractions with a specific molecular weight (MW). It is noteworthy that the great variety of methods for the determination of these forms of TE (with or without their isolation from the sample) greatly hinders the comparison of the results obtained by different investigators. Organic forms of different TE in sea water[53,105–109] and surface waters[110] have been observed.

These forms have been investigated in greatest detail for Cu, Hg, and Cr. It has been shown that, among the dissolved forms, the organic Cu fraction can amount to between 3 and 98% in marine waters[53,105–109,111–115] and 50% in surface waters.[116] On the basis of the analysis of EPR spectra, it has been suggested[117] that Cu is bound in these complexes to various reaction centres of the ligand via oxygen atoms. Mercury in the bound state amounts to 4–50% in sea water[53,63,83,84] and 27–100% in surface waters.[35,83,118] The vertical distribution of various forms of mercury in ocean waters is illustrated in Fig.1.[63] The following elements can exist in the organic form in sea water: Cr—45–60%,[85] Fe—12%, Mn—11%,[106] and Ni—up to 8%;[107] Se is present in the organic form to the extent of 40–60% in NW[119] and Pb is present in the organic form to the extent of 20–80% in river and estuary waters.[120] It is noteworthy that usually the highest concentrations of many TE are present in the organic fraction with MW = 10^3–10^4 (see, for example, Refs.63, 121, and 122). The role of organic matter in the binding of TE in NW[99,100] and the methods for the determination of the complexes formed,[3,7,10,123,124] as well as problems concerning the measurement of the complex-forming capacity and of the conventional stability constants for the ligands in NW[125] have been considered.

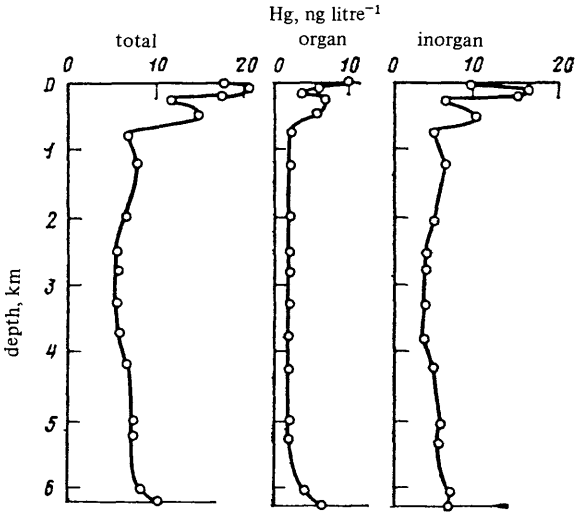


Figure 1. Vertical distribution of the different forms of mercury in the north western part of the Pacific Ocean.[63]

Among other dissolved physicochemical forms of TE, mention should be made of a labile form to which the free ion of the elements and labile complexes are usually assigned.[7,10] The concentrations of the labile mercury are 0.1–0.5 ng litre^{-1} in the Pacific Ocean[82] and 6–60 ng litre^{-1} in the North Sea.[126] The proportion of this form may correspond to the main bulk of the Mn in the <0.015 μm fraction in surface

waters.[127] The labile form is subdivided in its turn into the very labile, moderately labile, weakly labile, and inert forms.[128,129] This specification, which has a kinetic base, can be useful in the study of the biological accessibility of TE. It has been shown that Cd and Zn exist in river waters in more labile forms than Cu and Pb.[128] Overall, only a small proportion of the overall content of TE in NW corresponds to the labile fractions.

The forms of TE and their concentrations can vary greatly in oxygen-free deep waters, which exist, for example, in the Black and Baltic Seas and the fjords of Canada and Norway. The study of the vertical profiles of the dissolved TE in the Baltic Sea has shown that, on passing through the O_2–H_2S interface (the anoxic wedge), the Fe, Mn, and Co concentrations increase by a factor not less than 100 and there is a simultaneous increase of the Cu concentration by a factor not less than 100 and Zn, Cd, and Ni concentrations by a factor of 3–5 compared with oxidised waters.[130] The solubility of many TE is then controlled by the formation of disulphide and polysulphide complexes and the elements themselves exist in reduced forms, for example, Cu(I), Fe(II), and Mn(II). The Mn,[131,132] Fe, and Cr[131] redox cycles were investigated previously and it was shown, in particular, that the dissolved Mn(II) accumulates in deep anaerobic waters as a result of the reduction of the suspended MnO_2 when it is submerged via the anoxic wedge.

3. Chemical Forms of TE

The chemical forms of TE in SW have come to be determined only recently and a limited range of TE in different oxidation states (Cr, As, Sb, Se, and V) have now been investigated. It is noteworthy that the forms in the highest and lowest oxidation states predominate for each of the above TE in the oxidised and reduced SW respectively.

In sea and surface waters the concentration of inorganic Cr(VI) have been found to be 0.1–1.0 μg litre^{-1} [65,133–135] and 0.05–3.75 μg litre^{-1},[133,136] while those of inorganic Cr(III) are 0.002–1.0 μg litre^{-1} [65,85,133,135] and 0.20–2.36 μg litre^{-1}.[136] Vertical profiles have been obtained for these forms in ocean waters[64,85] and it has been shown that dissolved oxygen oxidises Cr(III) to the thermodynamically more stable Cr(VI), MnO_2 being a powerful catalyst of this process.[137] However, the ratio of the oxidised and reduced forms is not very well understood; it is believed that it is probably controlled kinetically.[138]

The following forms of As[30,31,139–143] and Sb[143–146] have been found in various types of SW (the two elements are designated by the general symbol E): E(III), E(V), MeE(V), and $Me_2E(V)$. Among the inorganic forms, E(V) predominates in the oxidised waters, while in the reduced waters the main form is E(III) and a sharp change in the ratio E(III)/E(V) is observed on passing the anoxic wedge,[143,147] owing to the reduction of E(V) and the possible formation of thiocomplexes.[143,146] In oxidised estuary waters, pronounced seasonal variations in the concentrations of the As forms have been noted;[142] in particular As(III) and the methyl forms of As are absent during the cold months at water temperatures below 9–12 °C probably owing to the sharp decrease of natural biomethylation.

The MeE(V) and $Me_2E(V)$ forms are encountered throughout the photic zone in the oceans but their proportion is only ~10% of the total content of the corresponding dissolved TE.[141,145] The vertical profiles of the chemical forms of As, Sb, and Ge in the Baltic Sea (where the anoxic wedge is at a depth of 170 m) (Table 5)[143] are controlled by biogeochemical cycles.

The concentrations of inorganic Se(IV) and Se(VI), which increase with the depth in the oceans, are in the range 4–64 and 40–120 ng litre^{-1} respectively.[148,149] In the oxygen-free sea water Se(-II) has been detected mainly in the form of Se-aminoacids and (or) peptides with the Se–C bond.[150] It has been shown that Se(IV) and Se(VI) are present in greater amounts in sea water than in surface water;[29,151] the opposite assertion is valid for Se(-II,0).[151] Among the different forms of vanadium, V(IV) and V(V) have been determined in river waters.[152]

Table 5. The vertical profiles of the chemical forms of As, Sb, and Ge (nmol litre^{-1}) in the Baltic Sea (the Gotland Depression).[143]

Depth, m	MeAs	Me_2As	As (III)	As (V)	MeSb
10	0.43	2.79	1.44	3.12	0.032
40	0.23	0.20	0.18	8.46	0.030
100	0.04	0.07	0.11	11.6	0.022
150	<0.04	0.07	0.18	13.2	0.019
175	0.06	0.15	12.3	2.63	0.013
200	0.08	0.21	11.2	3.55	0.034
215	0.04	0.24	10.7	3.30	0.032

Depth, m	Me_2Sb	Sb (III)	Sb (V)	MeGe *	Me_2Ge *
10	<0.006	0.008	0.56	78.4	54.5
40	<0.006	0.002	0.50	79.6	39.6
100	<0.006	0.003	0.31	94.3	54.6
150	<0.006	0.004	0.20	114	67.8
175	<0.006	0.008	0.25	88.2	54.3
200	<0.006	0.150	0.18	83.3	53.4
215	<0.006	0.137	0.18	108	75.3

*In pmol litre^{-1}.

The dominant dissolved forms of other important TE in certain oxidation states cannot be determined in NW with the aid of the analytical methods employed. They include Pb(II), Mn(II), Co(II), Ni(II), Fe(III), and Sn(IV).

Organoelemental compounds have now been found in NW only for Group IV and V and also mercury owing to the hydrolytic and oxidative instability of the element-carbon bonds for other TE. With rare exceptions, only the methyl derivatives of TE have been detected in NW, although thousands of tonnes of ethyl, butyl, and phenyl compounds of the most toxic TE (Hg, Pb, As, and Sn), some of which ultimately enter the NW, are produced annually by the chemical industry. However, these compounds are unstable and decompose in NW as a consequence of microbiological and chemical processes accompanied by the subsequent natural methylation with formation of methyl derivatives of TE (see Section VII).

The methyl compounds of As and Sn were examined above. Among the methylmercury derivatives, MeHg(II) has been found in the coastal sea waters of Japan at a concentration of 0.1 ng litre^{-1} [81] and in the river waters of Japan and Canada at concentrations in the range 2–8 ng litre^{-1},[93] which amounts to 1 and 30% respectively of the total content of mercury in these waters. In addition Me_2Hg at concentrations of 0–4 ng litre^{-1} has been detected in the surface waters of Japan.[153]

More detailed data have been compiled for Group IV elements. The methyl compounds of germanium have been found in the Sargasso and Bering Seas and also in the

river and estuary waters of the USA and Portugal at concentrations in the following ranges (ng litre^{-1}): Ge(IV)—0.4–12.3 and 0.6–7.4, MeGe(IV)—18.2–24.5 and 0–19.6, Me_2Ge(IV)—8–11.5 and 0–12, and Me_3Ge(IV)—0 and traces.[32] The vertical profiles for MeGe(IV) and Me_2Ge(IV) in the Baltic Sea are presented in Table 5.

The concentrations of methyltin derivatives in the rivers of the USA and Europe are indicated in Table 6. Only 5% of the total tin exists in the methyl form[154] but its content in the form of these compounds increases sharply in the polluted rivers of Florida (up to 54%)[33] and in the Rhine (up to 94%).[154] The following amounts of different tin derivatives have been found in the coastal waters and surface waters mainly in the USA and Canada (ng litre^{-1}): MeSn(IV)—0–42[33,155,156] and 0–1220,[33,52,56] Me_2Sn(IV)—0–200[33,155–157] and 0–400,[33,52,156] Me_3Sn(IV)—0–400[33,157] and 0–50,[33,52] and Me_4Sn—480 and 930.[157]

Table 6. The content of the chemical forms of tin (pmol litre^{-1}) in certain rivers of the USA and Europe.[154]

River	MeSn(IV)	Me_2Sn(IV)	Me_3Sn(IV)	Sn(inorg.)	Sn (total)
Colorado	traces	1.7	1.7	21.1	24.5
Mississippi	11.8	26.1	0.8	1036	1075
Ochlockonee	1.7	0.8	0.8	35.4	38.7
Rhine	592.3	1769	13.5	155	2530
Main	—	3.4	2.5	101.1	107

Large concentrations of butyl derivatives of tin have been detected in Lake Michigan and in the surface waters of Canada (ng litre^{-1}): BuSn(IV)—56–8480; Bu_2Sn(IV)—10–7300,[52,156] and Bu_3Sn(IV)—10–2910. The content of the last form in the rivers and lakes of Switzerland is only 1–15 ng litre^{-1}.[158] It is believed that these butyl compounds are of anthropogenic origin and enter NW as a result of, for example, leaching from the paint on boats and ships or as a result of transport through the atmosphere.[52] A difference has been discovered in the interaction of various forms of tin with inorganic and organic substances in NW.[159] The stability and degree of decomposition of organotin and organolead compounds under natural conditions in aqueous systems depend greatly on the number of organic groups linked to the metal.[160,161] Silicones at concentrations ranging from 2.0 to 54.2 μg litre^{-1} have been detected in the rivers of Japan.[162]

V. COLLOIDAL AND SUSPENDED PARTICLES

1. Composition, Properties, and Distribution of Particles

It has come to be assumed that filtration of samples of NW through membrane filters with a pore size of ~0.45 μm makes it possible to separate the suspended forms of any chemical ingredients from the dissolved forms. However, it has been frequently found that the dissolved forms usually contain fairly numerous submicron particles and organic macromolecules (see, for example, Refs.10, 163, 164), which are colloidal particles in terms of their size and whose origin, composition, and nature have so far been little investigated. It has been shown that the composition and content of 0.0012–0.4 μm colloidal particles isolated from river and estuary waters depend on the time of year and the salinity.[165] During the winter, fresh water colloids, which consist mainly of the products of continental erosion (argillaceous minerals and iron oxide), become enriched in carbon with increase of the salinity of water and their content falls sharply from 28.6 to 0.6 mg litre^{-1}. During the summer, these colloids are enriched mainly in carbon of biogenic origin and their concentration changes insignificantly, from 1.9 to 0.7 mg litre^{-1}, with increase of the salinity of water. According to data obtained by the pyrolysis of the organic fraction of these colloids, it is suggested that it consists mainly of the secretions and decomposition products of the phytoplankton and micro-organisms.[166] It has been shown[167] that the average content of colloidal carbon in coastal sea waters is 0.15 mg litre^{-1} regardless of the season, which corresponds to 11% of the total non-suspended carbon. It has been found that Fe(III) in river waters is present in the form of colloids stabilised by organic matter,[163,164,168,169] detergents, silicates, and phosphates, but not chlorides, nitrates, hydrogen carbonates, and sulphates.[169] The main bulk of colloidal Al is also coated by organic matter; the degree of adsorption of TE by these colloids depends on the stability of the complexes formed by the TE with organic ligands.[170]

The colloids in fresh water consist of electrically charged particles, whose charge is due to the presence of unsaturated and ruptured bonds on the surface of the crystal and the substitution of structural cations in the mineral lattice by cations in another valence state. The charge on the surfaces of inorganic colloids can be both positive (Al hydroxides at a high pH) and negative (quartz or argillaceous minerals), while in organic colloids (HS) it can only be negative. The negative charge of the colloids is balanced by binding the TE as a result of ion exchange, surface adsorption, and chelation.[99,171]

The content of the suspension in river waters varies from a fraction of a milligram to tens of grams per litre. Its average concentration in world rivers is ~0.5 g litre^{-1} and the maximum and minimum concentrations in the rivers of Asia and South America are 1.28 and 0.095 g litre^{-1} respectively.[172] In the waters of the open ocean its content is lower by several orders of magnitude: depending on the season, it changes by up to several hundreds of micrograms per litre in surface waters and is on average 10 μg litre^{-1} at depths in excess of 200 m.[173] The main bulk of the suspended particles have dimensions less than 10 μm in both river[94] and sea[173] waters, but the size of the biological particles formed in the ocean can reach 1 mm.[173]

The river suspension contains an amount of organic matter ranging from several tenths to 20%[172,174] while in ocean water it is 30–70%.[173] Quartz and argillaceous minerals (illite, chlorite, montmorillonite, and kaolinite) predominate in the terrigenous (mineral) river suspension,[172] while aluminosilicate particles, incorporating clay and non-aqueous minerals and also non-aluminosilicate minerals (quartz, pyrite, dolomite, barite, titanite, and iron and titanium oxides) predominate in coastal sea water.[175]

The main bulk of the suspension in surface ocean waters is of biological origin, consisting of carbonates, opal, and cellular and amorphous organic matter.[173,176] Its fraction is 60–90% of the total amount of the suspension entering deep waters down to 5000 m[177–180] (for example, the suspension collected in deep water traps contained 0–25% of clay, 60–70% of $CaCO_3$, 0–15% of opal, and 8–12% of organic carbon[180,181]), despite the fact that most of the suspension is mineralised and is consumed by hydrobionts following submersion.

The terrigenous component of the entire oceanic suspension is only 0.5–10%,[176] but, in contrast to the biogenic suspension, it does not dissolve and does not change in the bulk of the water and in sediments in water. A suspension of anthropogenic origin has been found in deep waters.[182]

It follows from data for the basic chemical composition of the suspensions in many world rivers[94,172] and also from the average compositions[172,183] that river suspensions occupy, in terms of their composition, an intermediate position between sedimentary rocks and soils. This indicates the source from which they originate. The basic chemical composition of a marine suspension has also been investigated.[184,185]

2. The Overall Content and Distribution of TE

Table 7 presents the content of certain TE in suspensions in the major world rivers. Among individual countries, this question has been most fully investigated in Japan, where 21 suspended TE have been determined in each of 166 rivers.[187] The highest concentrations in the suspension are usually those of Fe and Mn and in the Mississippi, for example, their contents reach 46.1 and 1.3 mg g^{-1} respectively.[87]

Table 7. The contents of TE in suspension in certain world rivers (μg g^{-1}).

River	Co	Cr	Cu	Ni	Pb	V	Zn	Refs.
Amazon	41	193	266	105	105	232	426	[183]
Congo	25	175	—	74	455	163	400	[183]
Ganges	14	71	30	80	—	—	163	[183]
Garonne	39	255	51	33	381	150	874	[183]
Mekong	20	102	107	99	113	175	300	[183]
Mississippi	21	72	42	55	45	—	184	[183]
Niger	40	150	60	—	—	180	—	[183]
Yangtze Kiang	25	83	70	78	65	—	108	[186]
Yellow River	12	72	33	38	35	—	75	[186]
Danube	16	140	189	89	—	—	322	[172]
Dnieper	5	86	90	93	—	90	260	[172]
Don	12	143	200	—	—	—	870	[172]
Volga	11	183	86	76	-	102	260	[172]

The contents of the suspended forms of TE in surface waters depend on the concentration of the suspension, its mineralogical and granulometric compositions, the climatic zone, and the time of year. Thus the concentrations of the suspended TE in various sections of the river proved to be inversely proportional to the content of the suspension in those sections,[188] while in Lake Ontario they were found to depend on the distance from the shore and amount on average to 50–80, 10–40, 20–60, and >60% of the overall concentrations of Cu, Ni, Cd, and Pb respectively.[189]

The contents of the suspended Hg and MeHg(II), which predominate during spring flooding, fall sharply during the summer period.[190]

It is impossible to say *a priori* which of the principal various forms of the TE, suspended or dissolved, is the main one in river waters. Al, whose suspended form always predominates, is an exception.[86,172,183] It has been shown that Fe and Mn,[86] Fe,[191,192] Fe, Mn, Ni, Co, Cr, and Pb,[183] and Cd, Pb, and Cu[193] predominate in the river suspensions; there is more than 90% of the Fe, Mn, Cd, Cr, Cu, Ni, Pb, and Zn in the suspension from the Mississippi[87] and more than 98% of the Hg from the Thames.[92] The relative importance of the suspended forms diminishes in the sequence Al > Fe > Mn > Co > Zn > Ni > Cu > Cd.[86] On the other hand, the dissolved form predominates for Ni, Cu, Zn, and Cd[86] and for Mn;[193,194] ~70% of Mn, Cu, and Zn and 100% of Cd[191] and more than 75% of Fe, Cd, Cu, and Zn[195] exist in this form. In order to arrive at correct conclusions from geochemical studies, it is desirable to carry out monthly measurements of the concentrations of these forms of TE in rivers over a period of many years.[86] Nevertheless one should note that the vast majority of TE are transported in rivers mainly in the suspended form.[88,172,183]

As a consequence of the low concentrations of the suspension in sea water and particularly ocean waters, they contain much smaller amounts of suspended TE than river waters. For example, the concentrations in the waters of the Central Atlantic are as follows (ng $litre^{-1}$): Al—78, Mn—3.5, Fe—222, Cr—3.1, Ni—1.8, Cu—3.6, Pb—4.5, and Zn—16;[22] the concentrations found in the Southern Indian Ocean are (in ng $litre^{-1}$ and μg g^{-1} respectively) Pb—35 and 260, Cd—3.5 and 26, Cu—100 and 730, and Zn—230 and 1700.[196] The suspended TE have also been determined in the waters of the Baltic Sea,[184] the Alaska Bay,[185,197] and in the plankton of the Pacific Ocean.[198] Turning now to individual TE, we may note that the concentrations of suspended mercury are (ng $litre^{-1}$) 0.2–0.3 in the coastal waters of Japan[84] and 0.5–0.9 in the Pacific Ocean and the Sea of Okhotsk[63] and those of suspended Cr are 80 in the Sea of Japan and 70 in the Pacific Ocean.[85] Pressure can exert a considerable influence on the interaction of the dissolved Al with the inorganic detritus in the bulk water, the bottom deposits, and at the water–deposit interface.[199] The importance of adsorption on the submerging organic suspension for the rapid decrease of the concentration of Hg in coastal sea waters has been emphasised.[122]

The proportions of the suspended forms of TE relative to their total content may be as follows: 3–10 for Hg,[63] 10–30 for Ag (Pacific Ocean),[61] and 1.7, 3.3, and 9.8% respectively for Zn, Cd, and Cu (Baltic Sea).[200]

The majority of the dissolved TE are finally removed into the deposit in the seas and oceans by becoming adsorbed on suspended particles. Biogenic particles formed initially in the surface layer from the phytoplankton and ultimately submerged into deep regions in the oceans in the form of detritus (the main bulk of which consists of fecal pellets whose rate of submersion ranges from several to thousands of metres per day) play an especially important role in controlling the distribution of TE in oceans.[1] A different fraction of each TE in the suspension is remineralised and passes to the bulk water, while another fraction of TE is found in pelagic clays and iron–manganese concretions and is then returned to surface waters by upwelling.

The rates of scavenging, which is an important factor limiting the concentrations of certain TE in oceans, and of the removal of TE from deep waters into deposits have been found.[181,201–203] For example, the rates are 20–50 μmol cm^{-2} g^{-1} for Mn and Fe and 0.1–0.4 μmol cm^{-2} g^{-1} for Cu, Co, Ni, Zn, V, and Sr.[203] The fluxes of suspended TE directed towards deep waters can undergo seasonal variations connected with the cyclic nature of the primary production,[202]

biogenic particles binding TE more strongly than mineral particles.[204]

3. Physicochemical Forms of TE

In a suspension TE can exist in stationary forms (the crystal lattice of undecomposed fragmented and argillaceous minerals) and mobile forms (surface sorption on organic matter and Fe and Mn hydroxides), only the latter being biologically accessible. It is noteworthy that there are at present no methods for the independent determination of the individual physicochemical forms of TE in a suspension, which seriously hinders comparison of the results obtained by different workers.[172, 205, 206]

The crystalline form and Fe and Mn hydroxides are usually most important in river suspensions.[172] For example, in the Amazon and Yukon rivers these forms comprise together 65–92% of Fe, Mn, Co, Cr, and Cu.[88] The predominance of both mobile[172,207] and organic and Mn hydroxides[207] forms has been noted for a series of TE. Differences between the ratios of different forms of TE in different granulometric fractions of the suspension have also been discovered.[207, 208]

In conformity with the significant difference between the compositions of river and marine suspensions noted above, it has been shown[209] that up to 70% of Al, Mn, Zn, Cu, Pb, and Li in the suspensions in the Indian Ocean exist in the adsorbed form and the form bound to Fe and Mn hydroxides and only 15% of these TE exist in the organic form, while in the inner seas the latter form reaches 30–70%, which is apparently associated with the vigorous absorption of the TE by the phytoplankton.

4. The Mechanisms of the Binding of TE

The suspended particles and deposits in aqueous media concentrate TE via three main mechanisms:[206] via their physicochemical adsorption from the bulk of the water, via their biological absorption, and via the sedimentation of the TE-enriched suspension. The degree of physicochemical adsorption, subdivided into physical and chemical, and also ion exchange[210] are influenced by the nature of the surface of the suspension or of the deposit in the aqueous medium.

The physicochemical adsorption of TE in different types of NW on the surfaces of clay, solid organic substances, and metal oxides is of greatest importance. Although previously very much more attention was devoted to the sorption of TE by clays, it is believed nowadays[206] that, in the adsorption of TE from NW, clays probably play the role of supports covered by organic matter or metal oxides. The surface of the clay will therefore not be considered here.

There exist three types of organic surfaces:[206] (1) the surfaces of living organisms such as bacteria and algae and, which is particularly important, the surface of marine plankton in which the main bulk of the TE are bound to non-skeletal organic phases and not to calcium carbonate and opal;[198] (2) the surface arising on decomposition of plant and animal matter and also on condensation of low-molecular-weight organic substances to form high-molecular-weight organic substances; it possesses many of the properties of polyelectrolytes and colloidal particles; (3) the surface formed by low-molecular-weight organic substances sorbed on clay or metal oxide supports.[211, 212]

Although the differences between these three types of organic surfaces have not been ultimately elucidated from the standpoint of the method of concentration of the TE by the latter, it has come to be assumed that salicylic acid is involved in the binding. The participation of carboxylic and phenolic functional groups[212,213] and also peptides[214] in the mechanism of the binding of TE has also been suggested.

We may note that the models of the reactions taking place on the surface in the absence of organic matter cannot be applied to natural systems, because in this case organic matter is adsorbed on the surface of the suspension,[213, 215] which is at least partly responsible for the negative electrostatic charge on almost all suspended particles.[211, 216] The amount of adsorbed organic matter then depends on the chemical composition of the surface of the suspension.[215]

Hydroxy-groups are present in water on the surfaces of metal oxides, the most important of which are Al_2O_3, FeOOH, and MnO_2.[4] The specific adsorption of cations and anions is therefore regarded as a result of their interaction with these groups at the water–oxide interface. The degree of binding of TE ions on the surface depends on the concentration of the reacting groups and the competing ions and also on the pH and the ionic strength of the medium.[206] Several mechanisms have been proposed to explain the sorption of TE,[217] including ion exchange, surface ionisation, and complex formation—in particular the formation of Zn and Pb phosphates.[218]

The picture becomes still more complex where one considers heterogeneous oxide surfaces, where the strengths of the bonds between TE and various centres can differ by an order of magnitude.[219] Hydrated oxide surfaces can adsorb organic matter also via ligand exchange. The degree of adsorption then depends on the pH and the MW.[206]

It must be emphasised that natural organic matter binding TE can be present in NW both in the dissolved state and in the form of a thin film coating the suspended particles. Natural organic matter can be regarded as the most important factor in the TE cycle in NW.[201, 205] This has been demonstrated for the waters of the open ocean where the distribution of the majority of TE is controlled by their biological absorption on the surface and their regeneration in deep waters from submerged biogenic residues.[1]

VI. ESTUARINE MIXING

Estuaries, which may be any water area where sea water mixes with the fresh water from the continental slope, namely river mouths, coastal bays, marshes, and basins behind a coastal bar constitute at the same time zones where there is a transition from the continent to the ocean and the continuity of the properties of the environment breaks down. A wide variety of hydrodynamic, physicochemical, and biological processes take place in estuaries at the geochemical river–sea barrier.

As a result of the sharp decrease of the flow rate of the river, estuarine mixing entails the deposition of more than 90% of the river suspension together with the TE bound to it.[172,220–223] Small particles whose size is less than 2–5 μm can be removed from the bulk of the water also as a result of the increase in their size as a consequence of coagulation, which arises on neutralisation or charge transfer involving clay particles, caused by the mixing of river waters with sea water, which is a strong electrolyte.

The concentrations of the inorganic and organic substances present in the suspended, colloidal, and dissolved states change sometimes very considerably, not only as a result of the mutual dilution of the fresh and sea waters but also as a consequence of various physicochemical transformations occurring under the non-steady conditions of the estuarine environment owing to the sharp changes over small distances

in salinity, pH, the content of the suspension, and other factors. Such transformations include precipitation, sorption, flocculation, complex formation, and other processes. The 2% isohaline is regarded as the hydrochemical boundary between the river and sea waters,[172] although the relative contents of the principal ions are almost constant only after 10% has been reached.

The causes of the observed variations in the content of both suspended and dissolved principal and trace elements in estuarine waters are not, however, altogether clear owing to the lack of complete hydrochemical and hydrodynamic information.[220,224] Sorption processes are frequently invoked to account for these causes. It has been shown that, among the principal cations, the Ca in the suspension exchanges for Na and to a lesser extent for K, while Mg is little involved in exchange reactions.[225] Among the TE, Fe,[226] Mn,[224,227] Cu,[224,228] Cd,[227,229] Pb,[120] and Ba, Co, Cs, and Zn[229] are desorbed into water. The increase in the concentrations of the dissolved TE, for example, Cu, is frequently attributed to their mobilisation from the resuspended deposits in aqueous media at high salinities[228] (for further details, see Section VII).

Overall, a clear idea about the role of sorption in estuarine processes is lacking. On the other hand, there is important evidence for the predominance of the influence of physical[224,230,231] (for example sedimentation and hydrological[230]) processes, and not physicochemical processes, on the chemical composition of the suspension in estuaries.

In the estuarine mixing of waters, the suspended or dissolved components behave conservatively when they participate only in a physical (mechanical) mixing process or non-conservatively when they are involved in various physicochemical reactions or in biological turnover. In the former case their concentrations depend linearly on the salinity and the input or removal of the components can therefore be estimated from the observed deviations from the straight line.[220]

An extremely important process for dissolved inorganic and organic substances in the estuary zone is their flocculation, i.e. their transformation into suspended amorphous particles, which takes place with increase of the salinity and pH of the water. The most important precondition for flocculation is the presence in river waters of dissolved Fe, which is believed, on the basis of a series of indirect data, to exist mainly in the form of Fe(III) hydroxides stabilised in the colloidal state by chemical binding to HA[99,163,168] (although recently objections have been raised against the latter hypothesis[232]). In the estuarine mixing of waters, the colloidal Fe and HA flocculate as a consequence of their destabilisation by cations from sea water.[163,168] However, it is not altogether clear whether this destabilisation of river colloids is associated with complete[163] or only partial[233] neutralisation of the negative charge. In contrast to Fe and HA, dissolved organic matter behaves conservatively.[164,168,233–235] The rate of flocculation increases with increasing salinity up to 15–18% and, for certain salinities, the bulk of the floccules are formed in the first 0.5 h after the start of mixing.[236,237]

Flocculation is the principal mechanism of the removal of dissolved TE from river water via coprecipitation and adsorption on the Fe hydroxide and HA floccules formed.[236,237] For example, TE can be removed from river water to the following extent:[236] 95% for Fe, 20% for Al, 40% for Cu and Ni, 25–45% for Mn, and 10% for Co. As[142] and Hg, Bi, and Sn[229] also flocculate. We may note that 65% of their HA is then lost, which, however, corresponds to only 3% of the dissolved organic matter.[168] The content of organic matter in river waters can be a regulating factor in the removal of TE;[238] the lanthanide elements are removed to the extent of 60–95% at a high concentration of organic matter and remain in the water at a low concentration. The removal of TE in the estuarine zone has been the subject of field observations.[115,163,172,224,239,240] The degree of removal can depend significantly on the form of the TE. For example, the inorganic colloidal form of Fe is removed quantitatively, while the organic form is removed only to the extent of 50%.[119] Estuaries behave as traps for TE in the course of their transfer from river to sea water, which may serve as one of the explanations of the relatively low concentrations of TE in the marine environment compared with the river environment.[241]. At the same time the conservative behaviour of Mn,[164,172,235] Cu,[115,242,243] Ni,[242,243] Cd and Zn,[242] and Cr[244] has been demonstrated. The form of the TE can strongly influence its behaviour: for example, compounds having the composition R_nPb (where R is an organic group) behave conservatively, while inorganic Pb behaves in the opposite manner.[245]

Overall, the geochemistry of the TE in estuaries, which depends also on their type and the physicogeographical conditions in the environment, is very complex and so far has been little investigated. The ideas concerning the behaviour and estimation of the losses of dissolved and suspended TE in various river estuaries are frequently contradictory and vary markedly. The atmospheric input of TE also has an effect.[246] Nevertheless it can be regarded as demonstrated that estuaries serve as traps for the majority of the dissolved and suspended substances on their way to the ocean.

VII. BOTTOM DEPOSITS AND PORE WATERS

1. Total Content and Distribution of TE

Marine, coastal, and estuarine deposits usually consist of two layers—the upper oxidised reddish-brown layer and the lower reduced olive-green layer. Variations in the thickness of the oxidised layer up to 1 mm depend on the input of organic matter on the bottom and on the rates of its decomposition (destruction). Oxygen diffuses downwards through the oxidised layer and the free H_2S, formed in the reduced layer by sulphate-reducing bacteria, diffuses upwards (sometimes without being evolved[247]). The reduced layer contains benthic organisms. It has been shown recently[248] that the colour transition from brown to green in marine deposits is accompanied by the reduction of Fe(III) to Fe(II) in pore waters.

In water areas with limited circulation, for example in the Black Sea and in fjords, oxygen does not reach deep waters and for this reason H_2S is present even near the bottom layer. In this case the deposits are coloured black and contain no benthic organisms.

The pore waters impregnating the bottom deposits always differ in their chemical composition from the water covering them (bottom water) by the fact that their concentrations of dissolved O_2 and SO_4^{2-} are reduced and those of bicarbonate are increased. Not only SO_4^{2-} may be reduced to H_2S but also CO_2 and NO_3^- may be reduced to CH_4 and NH_3 respectively in the pore waters of the reduced deposits.

As a consequence of the occurrence of diagenetic processes in ageing deposits, mainly in the pore waters, the chemical composition of the latter is important for the elucidation of the mechanism of the diagenesis. However, despite the fact that pore waters are usually enriched in the TE by a factor of 10 and more compared with the main bulk of the water, the contribution to the overall TE content in the wet deposit is insignificant (for the bibliography, see Warren[249]).

The bottom deposits are enriched in TE mainly as a result of three processes: (1) the sinking to the bottom of suspended particles; (2) the transfer of suspended particles along the bottom (in rivers); (3) the sorption of dissolved TE from water when the latter comes into contact with a deposit. The most important process is the sedimentation of the suspension in which one can isolate the detritus, biogenic, and deposited fractions. The particles of detritus contain TE within crystal lattices, in the adsorbed state on the surface, in the exchange centres of argillaceous minerals, and in surface layers formed by metal hydroxides or organic matter. Biogenic particles can contain TE within skeletal inorganic substances, in the adsorbed state on the surfaces, in exchange centres, in organic matter, in a bound form, and in the envelopes coating metal hydroxides. In the deposited fraction, which includes calcium carbonates and metal hydroxides and sulphides, the adsorbed TE are present on the surface.[249]

The content of TE in deposits from different water areas varies markedly, sometimes by 2–3 orders of magnitude, mainly in connection with the different degrees of their contamination. The concentration of TE in coastal,[250] lake and sea[249] deposits have been considered in a number of reviews. The contents of cadmium in deposits of different types have been analysed.[251] There exist data on the concentration of TE in river,[252,253] lake,[189,254] coastal,[197,255–264] and ocean[265] deposits.

The estuarine deposits, which behave as traps for the many suspended and dissolved TE carried out by the rivers, belong to the class of the most polluted. Their contents of some TE are listed in Table 8. The Rhine estuary and New Jersey river estuaries, whose deposits contain considerable concentrations of Pb and Cu, have attracted attention. The concentrations of As in the deposits in 27 estuaries in Great Britain differ by 3 orders of magnitude. In particular, its content in the Thames estuary is 4–6 μg g^{-1},[274] while its maximum concentration reaches 2500 μg g^{-1}.

Table 8. The average TE concentrations in estuarine deposits (μg/g of dry mass)

Estuary	Mn	Cu	Cd	Ni	Pb	Hg	Zn	Refs.
Ems	—	24	0.7	27	47	—	150	[266]
Rhine	—	99	5.0	31	213	—	870	[266]
Weser	—	42	2.4	58	154	—	393	[267]
St. Laurence	—	24	0.22	33	30	0.45	115	[268]
Miramichi	417	27	—	45	83	0.34	219	[269]
Ko-Jima	703	37	0.61	—	27	—	177	[270]
New Jersey rivers	—	66	2.24	36	128	0.66	218	[271]
Mersey	564	41	5.3	—	57	—	236	[272]
St. John	296	16	0.16	16	24	0.04	53	[273]

The distribution of mercury has been studied in particular detail in European countries. Thus its content in the deposits in more than 30 estuaries in Great Britain is 0.018–29 μg g^{-1},[275–279] while the deposits of 220 Swedish lakes contain 0.05–0.5 μg g^{-1} of mercury[280] although sewage had never been previously discharged into the lakes investigated. The mercury content in oceanic deposits is correlated with the underwater volcanic activity.[281]

The TE which have entered various water areas in a wide variety of ways—from the atmosphere, from rivers, from sewage discharges, etc.—inevitably accumulate in the bottom deposits. The bore cores of bottom deposits removed without disturbing the stratification can therefore reflect the entry of TE into the water basins over any period of time, up to 100 years. The geochronology of bottom deposits is usually determined by analysing the distribution of the ^{210}Pb isotope with respect to depth, but, in order to achieve a more accurate dating, combinations of different isotopes are employed, their number being fairly considerable (for example, ^{137}Cs, ^{238}Pu, $^{239,240}Pu$, ^{241}Am, and ^{244}Cm).[282]

The TE concentrations in the surface layers of lake, estuary, and coastal sea deposits in the vicinity of mining, industrial, and city regions can be a factor of 5–10 higher than 50–100 years ago, which indicates their anthropogenic origin. Apart from the information contained in a study mentioned previously,[16] there exist data on the geochronology of TE in the bottom deposits in fords,[283] lakes,[282,284–288] rivers,[282,289] estuaries,[290,291] fjords,[292–294] and coastal sea regions.[295–298] The historical record in the vertical Zn, Pb, Cr, Cu, As, Ni, Cd, and Hg profiles in the Rhine deposits over a period greater than 50 years is illustrated in Fig. 2.[289]

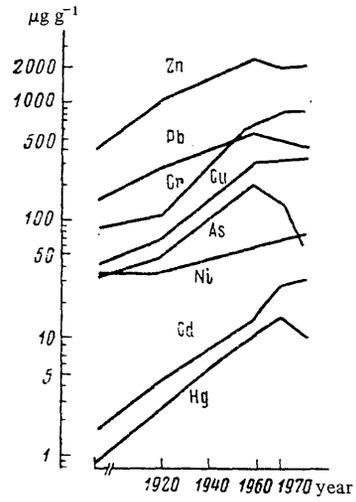


Figure 2. Time variation of the concentration of TE in the bottom deposits of the River Rhine.[289]

However, TE are distributed non-uniformly in deposits and their concentrations usually increase with decreased particle size.[249] The difference between the concentrations reaches in some cases an order of magnitude and more. The observed scatter can be appreciably reduced by employing different correction procedures.[15,299] A fraction whose size is less than 63 μm is usually analysed,[300] although it has been shown[299] that the content of many TE in a fraction up to 20 μm in size from estuarine deposits varies several times less from sample to sample than for a fraction whose size is up to 63 μm. Systematic investigation of different types of bottom deposits is therefore essential for a final selection of the fraction size most suitable for the monitoring of TE.

2. The Physicochemical and Chemical Forms of TE

The TE within bottom deposits are distributed between various physicochemical forms (geochemical fractions), which depend on Eh and pH[301] and differ in their mobility, leachability, and biological accessibility. In order to make it easier to understand the geochemical distribution of TE, the deposits are usually fractionated geochemically by methods involving single- or multi-stage consecutive extraction, which make it possible to leach selectively, with the aid of suitable chemical reagents, each of the identified fractions. The TE linked to the crystal lattice of silicate rocks are referred to as lithogenic and the corresponding fractions are called residual. The TE present in all the remaining geochemical fractions are referred to as non-lithogenic and the degree of pollution of the given deposit (water area) can be inferred from the level of their concentrations.

The single-stage extractions (they have been assessed and compared in a number of studies[302–304]) make it possible to determine either some one of the non-lithogenic TE fractions or their various combinations depending on the pH[305] and the reagent employed. In order to investigate more fully the physicochemical forms of TE, extractions comprising two,[289] three,[306] four,[272] five,[267, 303, 307] six,[308] and seven[15] steps are used. The advantages and disadvantages of the extraction methods have been discussed.[15, 302, 309, 310] It must be emphasised that the multistage consecutive extraction methods are not fully selective, the reactions being always influenced by factors such as, for example, the extraction time, temperature, the ratio of the volumes of the deposit and the extractant,[15, 309] and the readsorption of the TE.[311] Despite this, they are used widely.

Depending on the origin, composition, and degree of pollution of the deposit, the main bulk of the TE may be located in different geochemical fractions. The non-lithogenic TE are frequently bound to organic matter,[205, 269, 272, 308, 312, 313] which is particularly characteristic of mercury,[259, 275, 277, 278, 314] and also to the oxides of Fe (the main bulk of As[315–317]) and Mn,[205, 259, 308, 317–320] sulphides,[259, 313, 320] carbonates,[320–322] and phosphates.[319] Oceanic deposits have also been investigated.[317, 323]

Table 9. The physicochemical forms of TE (%) in the bottom deposits of the Rhine (A) and the Ems estuary (B).[15]

Forms	Zn		Ni		Cu		Pb		Cd
	A	B	A	B	A	B	A	B	A
Exchangeable	9	2	6	3	1	2	3	<1	18
Carbonate	37	31	13	10	28	19	52	35	38
Readily reducible	39	24	25	28	3	3	6	4	23
Moderately reducible	5	12	17	15	30	29	23	29	1
Non-silicate iron	1	2	6	—	2	5	6	11	—
Organic and sulphide	<1	3	3	6	4	3	<1	<1	6
Residual	9	26	40	38	32	39	10	20	14
Total concentration, μg g^{-1}	922	227	84	42	209	26	144	66	10

Examples of the application of the seven-stage extraction to deposits from the Rhine and from the Ems estuary are presented in Table 9,[15] whose data indicate an appreciable decrease of the proportion of the residual fraction for Zn, Cu, and Pb, despite the increase of their overall concentration, as a consequence of the pollution of the deposit. Appreciable amounts of Zn, Cu, Cd, and Pb are present in the carbonate fraction, while the proportion of the exchangeable form is appreciable only for cadmium.

With the exception of mercury, the chemical forms of TE have been little investigated in deposits. It has been shown that the MeHg(II) content in various estuarine and coastal deposits is usually less than 1% of the total Hg.[275, 278, 324] The MeHg(II) concentration is largely controlled by the content of sulphides and not of the total Hg and organic matter. At a specific concentration of sulphides, the level of MeHg(II) falls sharply, apparently as a consequence of a disproportionation reaction:

$$2\mathrm{MeHg(II)} + \mathrm{S^{2-}} \rightarrow (\mathrm{Me_2Hg})_2\mathrm{S} \rightarrow \mathrm{HgS} + \mathrm{Me_2Hg}.$$

The dimethylmercury formed vaporises and is transferred through the bulk water to the atmosphere.[279]

The predominance of a particular form of tin depends on the type of deposit.[155] In partly reduced and polluted marine deposits MeSn(IV) predominates, in oxidised and polluted deposits the main component is $Me_2Sn(IV)$, while in oxidised and unpolluted deposits $Me_3Sn(IV)$ is the main component. It has been shown[155] that the deposits from the Baltic and Mediterranean Seas contain 0.5 and 0 ng g^{-1} of the first form respectively, 0.3 and 2.6 ng g^{-1} of the second form respectively, and 0 and 8.6 ng g^{-1} of the third form respectively. The following butyltin derivatives have been detected in deposits from Canadian lakes (μg g^{-1}):[325] $BuSn(IV)$—0.013–0.58, $Bu_2Sn(IV)$—0.05–0.35, and $Bu_3Sn(IV)$—0.11–0.40. Mixed compounds, formed apparently as a result of methylation, have also been found: Bu_2SnMe_3—0.011–0.012 μg g^{-1} and Bu_3SnMe—0.011–0.023 μg g^{-1}. The deposits from Swiss lakes contain 0.002–0.016 μg g^{-1} of $Bu_3Sn(IV)$.[158] The river and coastal deposits were found to contain respectively 0.3–5.8 μg g^{-1} [162, 326] and 0.61 μg g^{-1} [326] of silicones.

3. Pore Waters

The concentration and distribution of TE and of their different forms in pore waters depend on Eh, pH, and the content and forms of organic matter and Fe and Mn compounds (amphoteric oxides, sulphides, carbonates, etc.). Pore waters constitute a medium in which TE are transported within surface deposits. The upper layer of these deposits 10–20 cm thick is most important for the exchange between deposits and the water near the bottom.[327] In marine deposits in the oxidised zone the concentrations of Mn and Ni are the same as in the water near the bottom, while in the Mn-reduced zone they are higher approximately by factors of 10 000 and 40 respectively.[328] The Cu content in oxidised pore waters is higher by a factor of 10 and more than in the water near the bottom.[328–330] This is due to the binding of copper by organic matter,[328, 330] which is also the cause of the increase in the Mo, V, and Cr concentrations in the reduced deposits with increase of depth.[331]

The pore waters in polluted deposits contain a particularly large amount of TE. For example, it was found that the pore waters in a lake contain approximately 0.15 mg litre^{-1} each of As(III) and As(V),[332] river pore waters were found to contain 5.85–6.88 g litre^{-1} of total As [including 6–10% of inorganic As and ~90% of $MeAsO(OH)_2$],[333] and the estuarine pore waters were found to contain 3.8 μg litre^{-1} of Hg.[334] In the last case an increase of the Cr, Cu, Zn, Pb, Ag, Ni, and Fe concentrations by a factor of 7.3–15 and of the Mn and Co concentrations by factors of 620 and

37 respectively compared with the water near the bottom was noted.[335] Large seasonal variations have been observed in the Fe, Mn, Cu and Mo contents.[336] The Fe, Cr, and Cu concentration profiles in the bottom water and in the pore waters of coastal marine deposits are presented in Fig. 3.[322]

4. The Remobilisation of TE

Under the influence of chemical changes in NW and microbiological processes in aqueous media, the TE present in bottom deposits can be remobilised and returned to the water. The remobilisation is induced by four types of chemical changes in water:[15] (1) by an increase of the concentrations of salts whose alkaline earth metal cations can compete with TE ions for sorption on particles; (2) by a change in the oxidation–reduction conditions, usually in connection with the decrease of the oxygen content as a consequence of increased eutrophication, whereupon Fe and Mn hydroxides dissolve, either partly or completely, owing to the reduction to Fe(II) and Mn(II) and some of the TE bound are then liberated (remobilisation of Mn, Cu, and Cd from partly reduced deposits with subsequent vertical transfer to the surface waters has been used to explain the increase in their concentrations in the shelf waters of Great Britain[337]); (3) by a decrease in pH, which leads to the dissolution of hydroxides and carbonates and also to an increase in the desorption of TE as a consequence of competition with H^+; it takes place either on oxidation of sulphides in uncontaminated surfactants or on precipitation of acid rain, which is characteristic of many lakes in Northern Europe and North America; in the latter case it has been shown[320] that Zn, Co, and Ni are remobilised mainly from the fraction of readily reducible deposits—Cd is remobilised from the organic phase, while Cu and Pb pass to water to only a slight extent; (4) by the increased employment of natural and synthetic complex forming agents, capable of forming soluble and stable complexes with TE, which would have otherwise been adsorbed on solid particles.

The biological remobilisation of TE can be achieved indirectly as a result of the activity of benthic organisms, which increase the ventilation of the deposits by the oxidised bottom waters[338, 339] and prevent thereby the formation of virtually insoluble sulphides of class B TE in pore waters.[340, 341]

The microbiological proesses in deposits where TE are bound to organic matter having a higher MW and a smaller number of functional groups as a result of diagenesis are more important. The remobilisation of TE takes place mainly in three principal ways:[15] (1) by the decomposition of the organic matter to compounds having a smaller MW but binding TE more effectively (see, for example, Graybeal and Heath[342]); (2) by the change in the physical properties of the medium, for example Eh and pH, as a consequence of metabolic activities; (3) by the conversion of inorganic TE compounds into organoelemental compounds.

5. Natural Methylation

Biomethylation is of greatest importance among the microbiological processes, since hitherto there has been no convincing proof of the biosynthesis of organoelemental compounds containing other alkyl or aromatic groups.[343] Apart from the experimental evidence for the biomethylation of TE in deposits described in reviews,[16,18,343,344] the biomethylation of As by fresh water green algae,[345] the methylation of Sn in estuary deposits,[157,346] and the methylation of Hg in the bulk of river,[347] lake,[348] and sea[349] waters have been observed recently. The seasonal variations in these processes[190,348] and the influence of sea salts on the formation and stability of MeHg(II) under aerobic and anaerobic conditions[350] and of the pH on the formation of methyl compounds of Hg and As[351] have been investigated.

The contents of the methyl derivatives of Hg, Sn, Pb, As, Sb, and Se in NW, in suspensions, and in deposits were indicated above in the appropriate Sections. In biological systems, in particular in micro-organisms, the methylating agents are Me–CoB_{12}, *S*-adenosylmethionine, and N^5-methyltetrahydrofolates. The mechanism of methylation by the $MeCOB_{12}$ reagent depends on the oxidation state of the TE and the reduction potential and can be electrophilic or radical.[18,343,352]

The biomethylation of TE is always accompanied by the reverse biodemethylation of their methyl derivatives,[16,344] which explains, in particular, the low concentrations of MeHg(II) in NW and deposits. The amount of mercury in this form is less than 1% of its total content.

However, one should note that by no means all biotransformations of TE have been elucidated. Thus, despite previous experimental data, the absence of the biomethylation of Pb[353] and Me_3SnCl[354] has been demonstrated recently. The compounds Me_4E (E = Sn or Pb), formed as a result of chemical disproportionation, for example, in the presence of sulphur compounds, have been detected:[354,355]

$$2Me_3E(IV) \xrightarrow{S^{2-}} (Me_3E)_2S \rightarrow Me_4E.$$

In river deposits HA and fulvoacids can also methylate Hg(II) to MeHg,[103,356] and, among the methylating agents forming part of their composition, the most powerful is

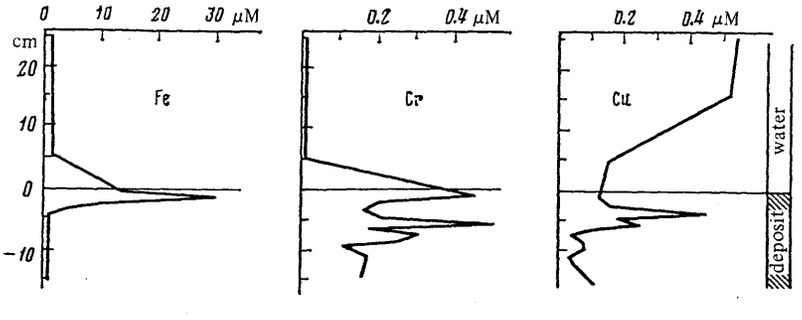


Figure 3. Vertical distribution of Fe, Cr, and Cu in the bottom water and the pore water of the coastal sediments in the Mediterranean.[322]

2,6-di-t-butyl-4-methylphenol and the weakest are mesitylene and *p*-xylene.[357]

In aqueous solutions MeHg(II) has been obtained from Hg(II) also in the presence of methanol, acetic and propionic acids, and aliphatic α-aminoacids (on photolysis), as well as a result of transmethylation:[18,343]

$$Me_3E(IV) + Hg(II) \rightarrow MeHg(II) + Me_2E(IV);\ E = Si, Sn, Pb.$$

The role of such reactions in the geochemical TE cycles is not altogether clear.

6. Iron–Manganese Concretions

In connection with the exploitation of the resources of the Pacific Ocean, the autogenic components of its bottom deposits, namely the iron–manganese concretions whose chemistry had been examined previously,[358] have become important. The results of the latest research into the role of TE and their forms in the concretions of the Pacific Ocean are described below.

The density of the concretions can reach 300 units per m^2 or 30 kg m^{-2}. Their dimensions are on average about 4 cm, but concretions up to 20 cm are encountered. They increase at an average rate from 30 to 300 mm in one million years.[359] Their Mn/Fe ratio varies from 5.6 to 70 and more than 99% of the Mn is in the form of Mn(IV),[360] although the main diagenetic source is probably Mn(II) formed from Mn(IV) in the vicinity of the deposit–water interface.[361] This process is part of the well investigated remobilisation of Mn from deposits,[328,330,362] which exerts a decisive influence on its distribution in bottom waters.

The concretions respond to this remobilisation by a faster increment in their volume on the side in contact with the deposit.[363] This side grows faster, compared with the upper part almost by a factor of 4.[359] A typical concretion consists of two separate non-detritus components having different compositions:[359] the bottom part is enriched in Mn, Mg, Ca, U, and Sb and the upper part in Fe, Ni, Cu, Zn, Co, Th, and the lanthanides. These differences in the chemical compositions of individual parts of the concretions are explained by the variable contributions of the following processes:[364] (1) the hydrogenic process which leads to the direct precipitation or accumulation of colloidal TE oxides from sea water; (2) oxidative diagenesis which takes place in oxidised deposits and tends to increase the content of TE in the concretion; (3) reductive diagenesis, which ensures the reduction of Mn(IV) to Mn(II) by the organic matter with its subsequent reoxidation to Mn(IV). Concretions have also been found in regions with very slow sedimentation of the suspension. In this case the increment in the mass of the concretions takes place at the expense of bottom waters with an increased content of suspended and dissolved TE brought there by bottom streams.[365]

The TE in concretions and also in a series of autogenic minerals (apatite, barite, opal, and carbonate) are mainly concentrated in the aluminosilicate and Mn and Fe oxide phases, owing to the characteristic features of the chemical forms of the TE in sea water and the physicochemical properties of these phases.[366] It has been shown that the TE in a concretion have different oxidation states—for example, Co(III), Pb(II), Pb(IV), and Ti(IV)[367] and Cu(II) and Ni(II).[368]

---o 0 o---

Significant advances have been made in recent years in the study of the forms of TE in natural aqueous media. The discovery of the relation between the forms of TE in the abiotic phases of natural aqueous media and their effect on hydrobionts is especially important. However, the experimental data to date are insufficient to reach definite conclusions about the influence of various forms of TE of anthropogenic origin on the health of specific water basins, which is one of the principal tasks of biogeochemistry.

REFERENCES

1. K.W.Bruland, in "Chemical Oceanography", Vol.8 (Edited by J.P.Riley and R.Chester), Acad.Press, London, 1983, p.398.
2. C.S.Wong, E.Boyle, K.W.Bruland, J.D.Burton, and E.D.Goldberg (Editors), "Trace Metals in Sea Water", Plenum Press, London, 1983, 920 pp.
3. T.M.Florence and G.E.Batley, CRC Critical Rev.Anal. Chem., 1980, **9**, 219.
4. W.Stumm and J.J.Morgan, "Aquatic Chemistry", Wiley, New York, 1981, 780 pp.
5. D.R.Turner, M.Whitfield, and A.G.Dickson, Geochim. Cosmochim.Acta, 1981, **45**, 855.
6. M.R.Hoffmann, Envir.Sci.Technol., 1981, **15**, 345.
7. A.K.Prokof'ev, Uspekhi Khim., 1983, **52**(3), 483 [Russ.Chem.Rev., 1983(3)].
8. P.N.Linnik and B.I.Nabivanets, Vodnye Resursy, 1980, 148.
9. M.Astruc, J.Lecomte, and P.Mericam, Envir.Techn. Letters, 1981, **2**, 1.
10. T.M.Florence, Talanta, 1982, **29**, 345.
11. S.J.De Mora and R.M.Harrison, Water.Res., 1983, **17**, 723.
12. G.E.Batley, in "Trace Element Speciation in Surface Waters and Its Ecological Implication (Edited by G.G.Leppard), Plenum Press, New York, 1983, p.17.
13. L.Brügmann, Sci.Total Envir., 1984, **37**, 41.
14. H.W.Nürnberg, Anal.Chim.Acta, 1984, **164**, 1.
15. U.Förstner and G.T.W.Wittmann, "Metal Pollution in the Aquatic Environment", Springer, Berlin, 1981, 486 pp.
16. A.K.Prokof'ev, Uspekhi Khim., 1981, **50**(1), 54 [Russ.Chem.Rev., 1981(1)].
17. W.R.Simpson, Prog.Oceanog., 1981, **10**, 1.
18. F.E.Brinckman and J.M.Bellama (Editors), "Organometals and Organometalloids. Occurrence and Fate in the Environment", ACS Symp.Ser.No.82, Amer. Chem.Soc., Washington, 1978, 447 pp.
19. P.J.Graig, in "Comprehensive Organometallic Chemistry", Vol.2 (Edited by G.Wilkinson, F.G.Stone, and E.W.Abel), Pergamon Press, New York, 1982, p.979.
20. L.L.Demina, "Formy Migratsii Tyazhelykh Metallov v Okeane" (The Forms in which Heavy Metals Migrate in the Ocean), Izd.Nauka, Moscow, 1982, 120 pp.
21. R.A.Duce, R.Arimoto, B.J.Ray, C.K.Unni, and P.J.Harder, J.Geophys.Res., 1983, **88C**, 5321.
22. P.Buat-Menard and R.Chesselet, Earth Planet.Sci. Letters, 1979, **42**, 399.
23. A.Z.Miklishanskii, Symposium, "Biogeokhimiya Okeana" (The Biogeochemistry of the Ocean) (Edited by A.S.Monin and A.P.Lisitsin), Izd.Nauka, Moscow, 1983, p.72.
24. A.Z.Miklishanskii, Yu.V.Yakovleva, B.V.Savel'ev, and V.V.Atrashkevich, Geokhimiya, 1981, p.927.
25. R.Chester, E.J.Sharples, K.Murphy, A.C.Saydam, and G.S.Sanders, Mar.Chem., 1983, **13**, 57.

26. D.M.Settle and C.C.Patterson, J.Geophys.Res., 1982, **87C**, 8557.
27. W.F.Fitzgerald, G.A.Gill, and A.D.Hewitt, see Ref.2, p.297.
28. J.Muhlbaier and G.T.Tisue, Water Air Soil Poll., 1981, **15**, 49.
29. G.A.Cutter, Anal.Chim.Acta, 1978, **98**, 59.
30. M.O.Andreae, Anal.Chem., 1977, **49**, 820.
31. D.Chakraborti, W.De Jonghe, and F.Adams, Anal. Chim.Acta, 1980, **120**, 121.
32. G.A.Hambrick III, P.N.Froelich, M.O.Andreae, and B.L.Lewis, Anal.Chem., 1984, **56**, 421.
33. R.S.Braman and M.A.Tompkins, Anal.Chem., 1979, **51**, 12.
34. D.Chakraborti, W.R.A.De Jonghe, W.E.Van Mol, R.J.A.Van Cleuvenbergen, and F.C.Adams, Anal. Chem., 1984, **56**, 2692.
35. K.Minagawa, Y.Takizawa, and I.Kifune, Anal.Chim. Acta, 1980, **115**, 103.
36. F.Slemr, W.Seiler, and G.Schuster, J.Geophys.Res., 1981, **86C**, 1159.
37. F.E.Brinckman, G.J.Olsen, and W.P.Iverson, in "Atmospheric Chemistry" (Edited by E.G.Goldberg, Springer, Berlin, 1982, p.231.
38. V.Hodge, S.R.Jouhson, and E.D.Goldberg, Geochem. J., 1978, **12**, 7.
39. G.P.Klinkhammer and M.L.Bender, Earth Planet.Sci. Letters, 1980, **46**, 361.
40. C.I.Measures, B.Grant, M.Khadem, D.S.Lee, and J.M.Edmond, Earth Planet.Sci.Letters, 1984, **71**, 1.
41. B.K.Schaule and C.C.Patterson, Earth Planet.Sci. Letters, 1981, **54**, 97.
42. A.R.Flegal and C.C.Patterson, Earth Planet.Sci. Letters, 1983, **64**, 19.
43. K.A.Hunter, Mar.Chem., 1980, **9**, 49.
44. Z.Jaworowski, M.Bysiek, and L.Kownacka, Geochim. Cosmochim.Acta, 1981, **45**, 2185.
45. J.T.Hardy, Prog.Oceanog., 1982, **11**, 307.
46. L.W.Lion and J.O.Leckie, Ann.Rev.Earth Planet. Sci., 1981, **9**, 449.
47. R.E.Pellenbarg, Estuar.Goast.Shelf Sci., 1984, **18**, 331.
48. A.W.Elzerman, D.E.Armstrong, and A.W.Andren, Envir.Sci.Technol., 1979, **13**, 720.
49. R.K.Barnes, G.E.Batley, and J.H.Sharp, Austral. J.Mar.Freshwater Res., 1982, **33**, 417.
50. L.W.Lion and J.O.Leckie, Limnol.Oceanogr., 1982, **27**, 111.
51. N.J.Pattenden, R.S.Cambray, and K.Playford, Geochim.Cosmochim.Acta, 1981, **45**, 93.
52. R.J.Maguire, Y.K.Chau, G.A.Bengert, E.J.Hale, P.T.S.Wong, and O.Kramar, Envir.Sci.Technol., 1982, **16**, 698.
53. G.T.Wallace, Mar.Chem., 1982, **11**, 379.
54. M.P.Bacon and A.W.Elzerman, Nature, 1980, **284**, 332.
55. H.W.Nürnberg, L.Mart, H.Rützel, and L.Sipos, Chem.Geol., 1983, **40**, 97.
56. K.Kremling, in "Methods of Seawater Analysis" (Edited by K.Grasshoff, M.Ehrhardt, and K.Kremling), Verlag Chemie, Weinheim, 1983, p.189.
57. M.S.Quinby-Hunt and K.K.Turekian, EOS, Trans. Amer.Geophys.Union, 1983, **64**, 130.
58. P.A.Yeast and J.A.Campbell, Mar.Chem., 1983, **12**, 43.
59. C.J.Jones and J.W.Murray, Limnol.Oceanog., 1984, **29**, 711.
60. G.A.Knauer, J.H.Martin, and R.M.Gordon, Nature, 1982, **297**, 49.
61. J.H.Martin, G.A.Knauer, and R.M.Gordon, Nature, 1983, **305**, 306.
62. R.M.Gordon, J.H.Martin, and G.A.Knauer, Nature, 1982, **299**, 611.
63. Y.Mijake and Y.Susaki, Deep-Sea Res., 1983, **30A**, 615.
64. R.E.Cranston, Mar.Chem., 1983, **13**, 109.
65. C.Jeandel and J.-F.Minster, Mar.Chem., 1984, **14**, 347.
66. J.H.Martin and G.A.Knauer, J.Mar.Res., 1982, **40**, 1213.
67. R.W.Collier, Nature, 1984, **309**, 441.
68. H.Elderfield and M.J.Greaves, Nature, 1982, **296**, 214.
69. E.A.Boyle, S.S.Huested, and S.P.Jones, J.Geophys. Res., 1981, **86C**, 8048.
70. K.W.Bruland and R.P.Franks, see Ref.2, p.395.
71. L.Mart, H.Rützel, P.Klahre, L.Sipos, U.Platzek, P.Valenta, and H.W.Nürnberg, Sci.Total Envir., 1982, **26**, 1.
72. M.J.Spenser, P.R.Betzer, and S.R.Piotrowicz, Mar. Chem., 1982, **11**, 403.
73. L.Brügmann, L.-G.Danielsson, B.Magnusson, and S.Westerlund, Mar.Chem., 1983, **13**, 327.
74. P.G.W.Jones, C.W.Baker, J.Olafsson, Coop.Res. Rep.No.125. Copenhagen: ICES, 1983, 33 pp.
75. K.Kremling and H.Petersen, Mar.Poll.Bull., 1984, **15**, 329.
76. F.Laumond, G.Copin-Montegut, P.Courau, and E.Nicolas, Mar.Chem., 1984, **15**, 251.
77. T.D.Jickless and A.H.Knap, Estuar.Coast.Shelf Sci., 1984, **18**, 245.
78. E.A.Boyle, D.F.Reid, S.S.Huested, and J.Hering, Earth Plant.Sci.Letters, 1984, **69**, 69.
79. L.-G.Danielsson and S.Westerlund, Mar.Chem., 1984, **15**, 273.
80. M.Nishimura, S.Konishi, K.Matsunaga, K.Hata, and T.Kosuga, J.Oceanog.Soc.Japan, 1983, **39**, 295.
81. J.Yamamoto, Y.Kaneda, and Y.Hikasa, Intern.J. Envir.Anal.Chem., 1983, **16**, 1.
82. N.S.Bloom and E.A.Crecelius, Intern.J.Envir.Anal. Chem., 1983, **14**, 49.
83. H.L.Windom and F.E.Tailor, Deep-Sea Res., 1979, **26A**, 283.
84. M.Fujita and K.Iwashima, Envir.Sci.Technol., 1981, **15**, 929.
85. E.Nakayama, H.Tokoro, T.Kuwamoto, and T.Fujinaga, Nature, 1981, **290**, 768.
86. P.A.Yeats and J.M.Bewers, Canad.J.Earth Sci., 1982, **19**, 982.
87. B.J.Presley, J.H.Trefry, and R.F.Shokes, Water Air Soil Poll., 1980, **13**, 481.
88. R.J.Gibbs, Geol.Sci.Amer.Bull., 1977, **88**, 829.
89. G.P.Klinkhammer and M.L.Bender, Estuar.Coast. Shelf Sci., 1981, **12**, 629.
90. A.C.Paul and K.C.Pillai, Water Air Soil Pollut., 1983, **19**, 63.
91. I.Sanemasa, E.Takagi, T.Deguchi, and H.Nagai, Anal.Chim.Acta, 1981, **130**, 149.
92. L.A.Nelson, Envir.Techn.Letters, 1981, **2**, 225.
93. A.Kudo, H.Nagase, and Y.Ose, Water Res., 1982, **16**, 1011.
94. E.T.Degens (Editor), "Transport of Carbon and Minerals in Major World Rivers", SCOPE/UNEP. Hamburg, 1982, Part 1, 765 pp.
95. E.K.Dursmaa and R.Dawson (Editors), "Marine Organic Chemistry", Elsevier, Amsterdam, 1981, 521 pp.

96. E.A.Romankevich, "Geochemistry of Organic Matter in the Ocean", Springer, New York, 1984, 340 pp.
97. B.Raspor, H.W.Nürnberg, P.Valenta, and M.Branica, Mar.Chem., 1984, **15**, 217.
98. G.R.Harvey, D.A.Boran, L.A.Chesal, and J.M.Tokar, Mar.Chem., 1984, **12**, 119.
99. J.H.Reuter and E.M.Perdue, Geochim.Cosmochim. Acta, 1977, **41**, 325.
100. R.F.C.Mantoura, see Ref.95, p.179.
101. K.S.Jackson, J.R.Jonasson, and G.B.Skippen, Earth-Sci.Rev., 1978, **14**, 97.
102. G.M.Varshal, T.K.Velyukhanova, I.Ya.Koshcheeva, V.A.Dorofeeva, N.S.Buachidze, O.G.Kosimova, and G.A.Makharadze, Zhur.Anal.Khim., 1983, 1590.
103. G.M.Varshal and N.S.Buachidze, Zhur.Anal.Khim., 1983, 2155.
104. B.Raspor, H.W.Nürnberg, P.Valenta, and M.Branica, Mar.Chem., 1984, **15**, 231.
105. J.R.Hasle and M.I.Abdullah, Mar.Chem., 1981, **10**, 487.
106. S.Hirata, J.Oceanog.Soc.Japan, 1983, **39**, 211.
107. A.K.Hauson and J.G.Quinn, Canad.J.Fish Aquat. Sci., 1983, **40**, suppl.2, 151.
108. D.J.Mackey, Mar.Chem., 1983, **13**, 169.
109. N.Takematsu, Y.Sato, and S.Okabe, J.Oceanog.Soc. Japan, 1983, **39**, 305.
110. C.Steinberg, Water Res., 1980, **14**, 1239.
111. K.Hirose, Y.Dokija, and Y.Sugimura, Mar.Chem., 1982, **11**, 343.
112. K.Kremling, A.Wenck, and C.Osterroht, Mar.Chem., 1981, **10**, 209.
113. D.L.Huizenga and D.R.Kester, Mar.Chem., 1983, **13**, 281.
114. C.M.G.Van den Berg, Mar.Chem., 1984, **14**, 201.
115. G.L.Mills and J.G.Quinn, Mar.Chem., 1984, **15**, 151.
116. K.Matsunaga, M.Negishi, S.Fukase, and K.Hasebe, Geochim.Cosmochim.Acta, 1980, **44**, 1615.
117. G.L.Mills, A.K.Hanson, J.G.Quinn, W.R.Lammela, and N.D.Chasteen, Mar.Chem., 1982, **11**, 355.
118. K.Kristotakis, P.Rubischung, and H.J.Tobschall, Fres.Z.Anal.Chem., 1979, **296**, 358.
119. K.Takajanagi and G.T.F.Wong, Mar.Chem., 1983, **14**, 141.
120. F.Elbaz-Poulichet, P.Holliger, W.W.Huang, and J.-M.Martin, Nature, 1984, **308**, 409.
121. M.R.Hoffmann, E.C.Yost, S.J.Eisenreich, and W.J.Maier, Envir.Sci.Technol., 1981, **15**, 655.
122. G.T.Wallace, D.L.Seibert, S.M.Holzknecht, and W.H.Thomas, Estuar.Coast.Shelf Sci., 1982, **15**, 151.
123. R.A.Saar and J.H.Weber, Envir.Sci.Technol., 1982, **16**, 510A.
124. Y.K.Chau and P.T.S.Wong, see Ref.2, p.87.
125. T.A.Neubecker and H.E.Allen, Water Res., 1983, **17**, 1.
126. L.Sipos, H.W.Nürnberg, P.Valenta, and M.Branica, Anal.Chim.Acta, 1980, **115**, 25.
127. D.P.H.Laxen, W.Davison, and C.Woof, Geochim. Cosmochim.Acta, 1984, **48**, 2107.
128. P.Figura and B.McDuffie, Anal.Chem., 1980, **52**, 1433.
129. J.A.Cox, K.Slonawska, D.K.Gatchell, and A.G.Heibert, Anal.Chem., 1984, **56**, 650.
130. K.Kremling, Mar.Chem., 1983, **13**, 87.
131. S.Emerson, R.E.Cranston, and P.S.Liss, Deep-Sea Res., 1979, **26A**, 859.
132. M.P.Bacon, P.G.Brewer, D.W.Spencer, J.W.Murray, and J.Goddard, Deep-Sea Res., 1980, **27A**, 119.
133. R.E.Cranston and J.W.Murray, Anal.Chim.Acta, 1978, **99**, 275.
134. G.J.De Jong and U.A.T.Brinkman, Anal.Chim.Acta, 1978, **98**, 243.
135. G.E.Batley and J.P.Matousek, Anal.Chem., 1980, **52**, 1570.
136. E.Orvini, T.Zerlia, M.Gallorini, and M.Speziali, Radiochem.Radioanal.Letters, 1980, **43**, 173.
137. E.Nakayama, T.Kuwamoto, S.Tsurubo, and T.Fujinaga, Anal.Chim.Acta, 1981, **130**, 401.
138. C.H.Van der Weijden, and M.Reitch, Mar.Chem., 1982, **11**, 565.
139. A.U.Shaikh and D.E.Tallman, Anal.Chim.Acta, 1978, **98**, 251.
140. M.O.Andreae, Deep-Sea Res., 1978, **25A**, 391.
141. M.O.Andreae, Limnol.Oceanog., 1979, **24**, 440.
142. A.G.Howard, M.H.Arbab-Zavar, and S.Apte, Estuar.Coast.Shelf Sci., 1984, **19**, 493.
143. M.O.Andreae and P.N.Froelich, Tellus, 1984, **36B**, 101.
144. M.O.Andreae, J.-F.Asmode, P.Foster, and L.Vant'dack, Anal.Chem., 1981, **53**, 1766.
145. M.O.Andreae, see Ref.2, p.1.
146. K.K.Bertine and D.S.Lee, see Ref.2, p.21.
147. M.L.Peterson and R.Carpenter, Mar.Chem., 1983, **12**, 295.
148. C.I.Measures, R.E.McDuff, and J.M.Edmond, Earth Planet.Sci.Letters, 1980, **49**, 102.
149. C.I.Measures, B.C.Grant, B.J.Mangum, and J.M.Edmond, see Ref.2, p.73.
150. G.A.Cutter, Science, 1982, **217**, 829.
151. H.Uchida, Y.Shimoishi, and K.Toei, Envir.Sci. Technol., 1980, **14**, 541.
152. E.Orvini, L.Lodola, E.Sabbioni, R.Pietra, and L.Goetz, Sci.Total Envir., 1979, **13**, 195.
153. S.Dogan and W.Haerdy, Intern.J.Envir.Anal.Chem., 1978, **5**, 157.
154. J.T.Byrd and M.O.Andreae, Science, 1982, **218**, 565.
155. S.Tugrul, T.I.Balkas, and E.D.Goldberg, Mar.Poll. Bull., 1983, **14**, 297.
156. V.F.Hodge, S.L.Seidel, and E.D.Goldberg, Anal. Chem., 1979, **51**, 1256.
157. J.-A.A.Jackson, W.R.Blair, F.E.Brinckman, and W.P.Iverson, Envir.Sci.Technol., 1982, **16**, 110.
158. M.D.Mueller, Fres.Z.Anal.Chem., 1984, **317**, 32.
159. M.Omar and H.J.M.Bowen, J.Radioanal.Chem., 1982, **74**, 273.
160. S.J.Blunden and A.H.Chapman, Envir.Techn.Letters, 1982, **3**, 267.
161. A.W.P.Jarvie, R.N.Markall, and H.R.Potter, Envir. Res., 1981, **25**, 241.
162. N.Watanabe, T.Nakamura, E.Watanabe, E.Sato, and Y.Ose, Sci.Total Envir., 1984, **35**, 91.
163. E.Boyle, J.M.Edmond, and E.R.Sholkovitz, Geochim. Cosmochim.Acta, 1977, **41**, 1313.
164. R.M.Moore, J.D.Burton P.J.LeB.Williams, and M.L.Joung, Geochim.Cosmochim.Acta, 1979, **43**, 919.
165. A.C.Sigleo and G.R.Helz, Geochim.Cosmochim.Acta, 1981, **45**, 2501.
166. A.C.Sigleo, T.C.Hoering, and G.R.Helz, Geochim. Cosmochim.Acta, 1982, **46**, 1619.
167. A.Zsolnay, Estuar.Coast.Mar.Sci., 1979, **9**, 559.
168. E.R.Sholkovitz, E.A.Boyle, and N.B.Price, Earth Planet.Sci.Letters, 1978, **40**, 130.
169. A.J.Cameron and P.S.Liss, Water Res., 1984, **18**, 179.
170. J.A.Davis, Geochim.Cosmochim.Acta, 1984, **48**, 679.

171. C.R.Olsen, N.H.Cutshall, and I.L.Larsen, Mar. Chem., 1982, **11**, 501.
172. V.V.Gordeev, "Rechnoi Stok v Okean i Cherty Ego Geokhimii" (River Drainage to the Ocean and Features of Its Geochemistry), Izd.Nauka, Moscow, 1983, 160 pp.
173. D.Lal, Science, 1977, **198**, 997.
174. V.E.Artem'ev, Litol.Polez.Iskop., 1981, 93.
175. P.E.Biscaye, C.R.Olsen, and G.G.Mathieu, Symposium, "Zashchita Morskoi Sredy ot Zagryazneniya. Trudy I Sovetsko-Amerikanskogo Simpoziuma" (Protection of the Marine Environment against Pollution. Proceedings of the Ist Soviet-American Symposium) (Edited by A.I.Simonov and A.K.Prokof'ev), Gidrometeoizdat, Leningrad, 1979, p.75.
176. A.P.Lisitsin and M.E.Vinogradova, see Ref.23, p.112.
177. G.A.Knauer, J.H.Martin and K.W.Bruland, Deep-Sea Res., 1979, **26A**, 97.
178. J.K.Bishop, R.W.Collier, D.R.Kettens, and J.M.Edmond, Deep-Sea Res., 1980, **27A**, 615.
179. S.Honjo, J.Mar.Res., 1980, **38**, 53.
180. S.Honjo, S.J.Manganini, and J.J.Cole, Deep-Sea Res., 1982, **29A**, 609.
181. P.G.Brewer, Y.Nozaki, D.W.Spencer, and A.P.Fleer, J.Mar.Res., 1980, **38**, 703.
182. J.Jedwab, Earth Planet.Sci.Letters, 1980, **49**, 551.
183. J.-M.Martin and M.Meybeck, Mar.Chem., 1979, **7**, 173.
184. K.Boström, J.-O.Burman, C.Ponter, and J.Ingri, Mar.Chem., 1981, **10**, 335.
185. R.A.Feely, G.J.Massoth, and W.M.Landing, Mar. Chem., 1981, **10**, 431.
186. Y.-H.Li, H.Teraoka, T.-S.Yang, and J.-S.Chen, Geochim.Cosmochim.Acta, 1984, **48**, 1561.
187. H.Teraoka and J.Kobayashi, Geochim.J., 1980, **14**, 203.
188. M.M.Reddy, K.V.Krishnamurty, E.Shpirt, G.A.Carlson, and L.Hetling, Envir.Internat., 1982, **7**, 315.
189. J.O.Nriagu, H.K.T.Wong, and R.D.Coker, Water Res., 1981, **15**, 91.
190. T.A.Jackson, J.W.Parks, P.D.Jones, R.N.Woychuk, J.A.Sutton, and J.D.Hollinger, Hydrobiology, 1982, **92**, 473.
191. B.T.Hart, S.H.R.Davies, and P.A.Thomas, Water. Res., 1982, **16**, 605.
192. A.J.Pik, J.M.Eckert, and K.L.Williams, Austral.J. Mar.Freshwat.Res., 1982, **33**, 971.
193. D.P.H.Laxen and R.M.Harrison, Sci.Total Envir., 1981, **19**, 59.
194. D.P.H.Laxen and R.M.Harrison, Water Res., 1981, **15**, 1053.
195. B.T.Hart and S.H.R.Davies, Estuar.Coast.Shelf Sci., 1981, **12**, 353.
196. J.E.Harris and G.J.Fabris, Mar.Chem., 1979, **8**, 163.
197. W.M.Landing and R.A.Feely, Deep-Sea Res., 1981, **28A**, 19.
198. R.Collier and J.Edmond, Prog.Oceanog., 1984, **13**, 113.
199. R.M.Moore and G.E.Millward, Geochim.Cosmochim. Acta, 1983, **47**, 235.
200. K.Kremling and H.Petersen, Mar.Chem., 1978, **6**, 155.
201. L.S.Balistrieri, P.G.Brewer, and J.W.Murray, Deep-Sea Res., 1981, **28A**, 101.
202. T.D.Jickells, W.G.Deuser, and A.H.Knap, Deep-Sea Res., 1984, **31A**, 1169.
203. J.Thomson, M.S.N.Carpenter, S.Colley, T.R.S.Wilson, H.Elderfield, and H.Kennedy, Geochim.Cosmochim. Acta, 1984, **48**, 1935.
204. L.S.Balistrieri and J.W.Murray, Geochim.Cosmochim. Acta, 1984, **48**, 921.
205. L.W.Lion, R.S.Altmann, and J.O.Leckie, Envir.Sci. Technol., 1982, **16**, 660.
206. B.T.Hart, Hydrobiologia, 1982, **91**, 299.
207. V.V.Gordeev, A.Yu.Mitropol'skii, and O.V.Turkina, Geokhimiya, 1984, 1461.
208. V.N.Oreshkin and V.V.Gordeev, Geokhimiya, 1983, 603.
209. L.L.Demina, E.N.Shumilin, and S.B.Tambiev, Geokhimiya, 1984, 565.
210. U.Förstner and W.Salomons, see Ref.12, p.245.
211. J.A.Davis and R.Gloor, Envir.Sci.Technol., 1981, **15**, 1223.
212. E.Tipping, Geochim.Cosmochim.Acta, 1981, **45**, 191.
213. K.A.Hunter, Limnol.Oceanog., 1980, **25**, 807.
214. B.T.Hart, Envir.Techn.Letters, 1981, **2**, 95.
215. J.A.Davis, Geochim.Cosmochim.Acta, 1982, **46**, 2381.
216. E.Tipping and D.Cooke, Geochim.Cosmochim.Acta, 1982, **46**, 75.
217. J.Westall and H.Hohl, Adv.Coll.Interface, 1980, **12**, 265.
218. S.B.Bradley and J.Lewin, Envir.Poll., 1982, **4B**, 257.
219. M.B.Benjamino and J.O.Leckie, J.Coll.Interface Sci., 1981, **79**, 209.
220. E.Olaussen and I.Cato (Editors), "Chemistry and Biochemistry of Estuaries", Wiley, New York, 1980, 452 pp.
221. J.-M.Martin and M.Whitfield, see Ref.2, p.265.
222. J.C.Duinker, see Ref.2, p.209.
223. E.R.Sholkovitz and N.B.Price, Geochim.Cosmochim. Acta, 1980, **44**, 163.
224. V.V.Gordeev, V.A.Chudaeva, and V.M.Shul'kin, Litol.Polezn.Iskop., 1983, 99.
225. F.L.Sayles and P.C.Mangelsdorf, Geochim.Cosmochim. Acta, 1979, **43**, 767.
226. W.K.Fletcher, G.S.Holmes, and A.G.Lewis, Mar. Chem., 1983, **12**, 195.
227. A.J.Paulson, R.A.Feely, H.C.Curl, and J.F.Gendron, Water Res., 1984, **18**, 633.
228. H.Windom, G.Wallace, R.Smith, N.Dudek, M.Maeda, R.Dulmage, and F.Storti, Mar.Chem., 1983, **12**, 183.
229. Y.-H.Li, L.Burkhardt, and H.Teraoka, Geochim. Cosmochim.Acta, 1984, **48**, 1879.
230. E.R.Sholkovitz, Estuar.Coast.Mar.Sci., 1979, **8**, 523.
231. J.E.Rae and S.R.Aston, Water Res., 1982, **16**, 649.
232. L.E.Fox, Geochim.Cosmochim.Acta, 1984, **48**, 879.
233. K.A.Hunter, Geochim.Cosmochim.Acta, 1983, **47**, 467.
234. K.A.Hunter and P.S.Liss, Limnol.Oceanog., 1982, 27, 322.
235. K.W.Eastman and T.M.Church, Estuar.Coast.Shelf Sci., 1984, **18**, 447.
236. E.R.Sholkovitz, Eart Planet.Sci.Letters, 1978, **41**, 77.
237. E.R.Sholkovitz and D.Copland, Geochim.Cosmochim. Acta, 1979, **43**, 181.
238. J.Hoyle, H.Elderfield, A.Gledhill, and M.Greaves, Geochim.Cosmochim.Acta, 1984, **48**, 143.
239. D.Eisma, J.Kalf, and M.Veenhuis, Netherl.J.Sea. Res., 1980, **14**, 172.
240. J.H.Sharp, C.H.Culberson, and T.M.Church, Limnol. Oceanog., 1982, **27**, 1015.
241. J.Schoer, Y.T.Hong, and U.Förstner, Envir.Techn. Letters, 1983, **4**, 277.
242. L.-G.Danielsson, B.Magnusson, S.Westerlund, and K.Zhang, Estuar.Coast.Shelf Sci., 1983, **17**, 73.

243. E.A.Boyle, S.S.Huested, and B.Grant, Deep-Sea Res., 1982, **29A**, 1355.
244. J.A.Campbell and P.A.Yeats, Estuar.Coast.Shelf Sci., 1984, **19**, 513.
245. J.P.Riley and J.V.Towner, Mar.Poll.Bull., 1984, **15**, 153.
246. M.Owens, Mar.Poll.Bull., 1984, **17**, 41.
247. T.Masuzawa and Y.Kitano, J.Oceanogr.Soc.Japan, 1983, **39**, 171.
248. M.Lyle, Limnol.Oceanog., 1983, **28**, 1026.
249. L.J.Warren, Envir.Poll., 1981, **2B**, 401.
250. A.Katz and I.R.Kaplan, Mar.Chem., 1981, **10**, 261.
251. U.Förstner, Experientia, 1984, **40**, 23.
252. C.B.Dissanayake, H.J.Tobschall, H.Palme, U.Rast, and B.Spettel, Sci.Total.Envir., 1983, **29**, 243.
253. F.Tada, H.Nishida, M.Miyai, and E.Suzuki, Envir. Geol., 1983, **4**, 217.
254. J.Hamilton-Taylor, Sci.Techn.Letters, 1983, **4**, 115.
255. M.H.Bothner, P.J.Aruscavage, W.M.Ferrebee, and P.A.Baedecker, Estuar.Coast.Mar.Sci., 1980, **10**, 523.
256. A.L.Meyerson, G.W.Luther, J.Krajewski, and P.I.Hires, Mar.Poll.Bull., 1981, **12**, 244.
257. P.F.Larsen, V.Zdanowicz, A.C.Johnson, and L.F.Doggett, Chem.Ecol., 1983, **1**, 191.
258. V.Talbot and A.Chegwidden, Envir.Poll., 1983, **5B**, 187.
259. D.H.Loring, Canad.J.Earth.Sci., 1982, **19**, 930.
260. R.Donazzolo, O.Hieke Merlin, L.Menegazzo Vitturi, and B.Pavoni, Mar.Poll.Bull., 1984, **15**, 93.
261. S.A.Sinex and G.R.Helz, Envir.Geol., 1981, **3**, 315.
262. P.Harbison, Mar.Geol., 1984, **61**, 221.
263. P.S.Roy and E.A.Crawford, Estuar.Coast.Shelf Sci., 1984, **19**, 341.
264. J.G.Farmer, Mar.Envir.Res., 1983, **8**, 1.
265. M.Lew, Chem.Geol., 1981, **33**, 205.
266. W.Salomons and W.G.Mook, Neth.J.Sea Res., 1977, **11**, 119.
267. W.Calmano, S.Wellershaus, and U.Förstner, Envir. Techn.Letters, 1982, **3**, 199.
268. D.H.Loring, Canad.J.Earth.Sci., 1978, **15**, 757.
269. J.D.Willey and R.A.Fitzgerald, Canad.J.Earth.Sci., 1980, **17**, 254.
270. I.Aoyama, Y.Urakaini, and O.Kawara, Envir.Poll., 1982, **4B**, 27.
271. W.H.Renwick and H.M.Edenborn, Envir.Poll., 1983, **5B**, 175.
272. M.A.Badri and S.R.Aston, Envir.Poll., 1983, **6B**, 181.
273. S.Ray and S.D.Macknight, Mar.Poll.Bull., 1984, **15**, 12.
274. W.J.Langstone, J.Mar.Biol.Ass.U.K., 1980, **60**, 869.
275. P.D.Bartlett and P.J.Craig, Water Res., 1981, **15**, 37.
276. G.E.Millward and I.Herbert, Envir.Poll., 1981, **2B**, 265.
277. J.E.Rae and S.R.Aston, Mar.Poll.Bull., 1981, **12**, 367.
278. W.J.Langstone, J.Mar.Biol.Ass.U.K., 1982, **62**, 667.
279. P.J.Craig and P.A.Moreton, Mar.Poll.Bull., 1983, **14**, 408.
280. I.Björklund, H.Borg, and K.Johansson, Ambio, 1984, **13**, 118.
281. M.E.Cox and G.M.McMurtry, Nature, 1981, **289**, 789.
282. R.J.Breteller, V.T.Bowen, D.L.Schneider, and R.Henderson, Envir.Sci.Technol., 1984, **18**, 404.
283. M.Thomas, D.Petit, and L.Lamberts, Water Air Soil Poll., 1984, **23**, 51.
284. J.O.Nriagu, A.L.W.Kemp, H.K.T.Wong, and N.Harper, Geochim.Cosmochim.Acta, 1979, **43**, 247.
285. J.Hamilton-Taylor, Envir.Sci.Technol., 1979, **13**, 693.
286. J.Dominik, A.Mangini, and F.Prosi, Envir.Geol., 1984, **5**, 151.
287. E.R.Christensen and N.-K.Chien, Envir.Sci.Technol., 1981, **15**, 553.
288. B.Rippey, R.J.Murphy, and S.W.Kyle, Envir.Sci. Technol., 1982, **16**, 23.
289. W.Salomons and A.J.De Groot, in "Environmental Biogeochemistry", Vol.1 (Edited by W.E.Krumbein), Ann.Arbor Sci.Publ., 1978, p.149.
290. E.D.Goldberg, J.J.Griffin, V.Hodge, M.Koide, and H.Windom, Envir.Sci.Technol., 1979, **13**, 588.
291. G.T.F.Wong and C.S.Moy, Estuar.Coast.Shelf.Sci., 1984, **18**, 37.
292. C.Barbeau, R.Bougie, and J.-E.Cote, Canad.J.Earth Sci., 1981, **18**, 1065.
293. J.Skei and P.E.Paul, Geochim.Cosmochim.Acta, 1979, **43**, 239.
294. J.N.Smith and D.H.Loring, Envir.Sci.Technol., 1981, **15**, 944.
295. A.Hoshika and T.Shiozawa, J.Oceanog.Soc.Japan, 1984, **40**, 115.
296. Y.Kitano, M.Sakata, and E.Matsumoto, J.Oceanog. Soc.Japan, 1981, **37**, 259.
297. L.K.Benninger, R.C.Aller, J.K.Cochran, and K.K.Turekian, Earth Planet.Sci.Letters, 1979, **43**, 241.
298. Y.Kitano, M.Sakata, and E.Matsumoto, Geochim. Cosmochim.Acta, 1980, **44**, 1279.
299. F.Ackermann, H.Bergmann, and U.Schleichert, Envir.Techn.Letters, 1983, **4**, 317.
300. U.Förstner and W.Salomons, Envir.Tech.Letters, 1980, **1**, 494.
301. R.P.Gambrell, R.A.Khalid, and W.H.Patrick, Envir.Sci.Technol., 1980, **14**, 431.
302. S.N.Luoma and G.W.Bryan, Sci.Total Envir., 1981, **17**, 165.
303. R.Van Valin and J.W.Morse, Mar.Chem., 1982, **11**, 535.
304. B.Cosma, V.Contardy, G.Zanicchi, and R.Capelli, Chem.Ecol., 1983, **1**, 331.
305. J.H.Trefry and S.Metz, Anal.Chem., 1984, **56**, 745.
306. W.Salomons and U.Förstner, Envir.Techn.Letters, 1980, **1**, 506.
307. A.Tessier, P.G.C.Campbell, and M.Bisson, Anal. Chem., 1979, **51**, 844.
308. Y.Hong and U.Förstner, Geochemistry, 1984, **3**, 37.
309. B.Welte, N.Bles, and A.Montiel, Envir.Techn.Letters, 1983, **4**, 79.
310. U.Förstner, Fres.Z.Anal.Chem., 1983, **316**, 604.
311. P.S.Rendell, G.E.Batley, and A.J.Cameron, Envir. Sci.Technol., 1980, **14**, 314.
312. F.Tada and S.Suzuki, Water Res., 1982, **16**, 1489.
313. L.H.Filipek and R.M.Owen, Chem.Geol., 1979, **26**, 105.
314. F.Baldi and R.Bargagli, Mar.Envir.Res., 1982, **6**, 69.
315. C.Neal, H.Elderfield, and R.Chester, Mar.Chem., 1979, **7**, 207.
316. W.A.Maher, Chem.Geol., 1984, **47**, 333.
317. H.Kunzendorf, P.Walter, P.Stoffers, and R.Gwozdz, Mar.Chem., 1984, **47**, 113.
318. D.H.Loring, Canad.J.Earth Soc., 1979, **16**, 1196.
319. C.Houba, J.Remacle, D.Dubois, and J.Thorez, Water Res., 1983, **17**, 1281.

320. U.Förstner, Hydrobiologia, 1982, **91**, 269.
321. P.Dossis and L.J.Warren, Envir.Sci.Technol., 1981, **15**, 1451.
322. F.Rapin, G.P.Nembrini, U.Förstner, and J.I.Garcia, Envir.Techn.Letters, 1983, **4**, 387.
323. V.N.Lukashin, see Ref.23, p.312.
324. J.A.J.Thompson, R.W.Macdonald, and C.S.Wong, Geochim.J., 1980, **14**, 71.
325. R.J.Maguire, Envir.Sci.Technol., 1984, **18**, 291.
326. R.Pellenbarg, Envir.Sci.Technol., 1979, **13**, 565.
327. G.P.Nembrini, F.Rapin, J.I.Garcia, and U.Förstner, Envir.Techn.Letters, 1982, **3**, 545.
328. G.P.Klinkhammer, Earth Planet.Sci.Letters, 1980, **49**, 81.
329. G.P.Klinkhammer, D.T.Heggie, and D.W.Graham, Earth Planet.Sci.Letters, 1982, **61**, 211.
330. J.J.Sawlan and J.W.Murray, Earth Planet.Sci. Letters, 1983, **64**, 213.
331. H.J.Brumsack and J.M.Gieskes, Mar.Chem., 1983, **14**, 89.
332. J.Aggett and R.Kadwani, Analyst, 1983, **108**, 1495.
333. D.G.Iverson, M.A.Anderson, T.R.Holm, and R.R.Stanforth, Envir.Sci.Technol., 1979, **13**, 1491.
334. M.H.Bothner, R.A.Jahnke, M.L.Peterson, and R.Carpenter, Geochim.Cosmochim.Acta, 1980, **44**, 273.
335. H.Teraoka and M.Ogawa, Japan.J.Limnol., 1984, **45**, 6.
336. M.E.Hines, W.B.Lyons, P.V.Armstrong, W.H.Orem, M.J.Spencer, H.E.Gandette, and G.E.Jones, Mar. Chem., 1984, **15**, 173.
337. K.Kremling, Nature, 1983, **303**, 225.
338. S.Emerson, R.Jahnke, and D.Heggie, J.Mar.Res., 1984, **42**, 709.
339. C.D.Hunt and D.L.Smith, Canad.J.Fish.Aquat.Res., 1983, **40**, suppl.2, 132.
340. H.Elderfield, P.J.McCaffrey, N.Luedtke, M.Bender, and V.W.Truesdale, Amer.J.Sci., 1981, **281**, 1021.
341. L.Jacobs and S.Emerson, Earth Planet.Sci.Letters, 1982, **60**, 237.
342. A.L.Graybeal and G.R.Heath, Geochim.Cosmochim. Acta, 1984, **48**, 965.
343. J.S.Thayer and F.E.Brinckman, in "Advances in Organometallic Chemistry", Vol.20 (Edited by F.G.A.Stone and R.West), Acad.Press, New York, 1982, p.313.
344. P.J.Craig, in "The Handbook of Environmental Chemistry", Vol.1, Part A (Edited by O.Hutzinger), Springer, New York, 1980, p.169.
345. M.D.Baker, P.T.S.Wong, Y.K.Chau, C.I.Mayfield, and W.E.Inniss, Canad.J.Fish.Aquat.Sci., 1983, **40**, 1254.
346. L.E.Hallas, J.C.Means, and J.J.Cooney, Science, 1981, **215**, 1505.
347. J.W.M.Rudd, M.A.Turner, A.Furutani, A.L.Swick, and B.E.Townsed, Canad.J.Fish.Aquat.Sci., 1983, **40**, 2206.
348. A.Furutani and J.W.M.Rudd, Appl.Envir.Microbiol., 1980, **40**, 770.
349. G.Topping and I.M.Davies, Nature, 1981, **290**, 243.
350. G.Compeau and R.Bartha, Bull.Envir.Contam.Toxicol., 1983, **31**, 486.
351. M.D.Baker, W.E.Inniss, C.I.Mayfield, P.T.S.Wong, and Y.K.Chau, Envir.Techn.Letters, 1983, **4**, 89.
352. Y.T.Fanchiang, W.P.Ridley, and J.M.Wood, Adv. Inorg.Biochem., 1979, 1, 147.
353. A.W.P.Jarvie, A.P.Whitmore, R.N.Markall, and H.R.Potter, Envir.Poll., 1983, **6B**, 81.
354. P.J.Craig and S.Rapsomanikis, Envir.Techn.Letters, 1984, **5**, 407.
355. A.W.P.Jarvie, A.P.Whitmore, R.N.Markall, and H.R.Potter, Envir.Poll., 1983, **6B**, 69.
356. H.Nagase, Y.Ose, T.Sato, and T.Ishikawa, Sci. Total Envir., 1982, **25**, 133.
357. H.Nagase, Y.Ose, T.Sato, and T.Ishikawa, Sci. Total Envir., 1984, **32**, 147.
358. I.I.Volkov, in "Khimiya Okeana" (The Chemistry of the Ocean), Vol.2 (Edited by I.I.Volkov), Izd. Nauka, Moscow, 1979, p.414.
359. B.Finney, G.R.Heath, and M.Lyle, Geochim.Cosmochim.Acta, 1984, **48**, 911.
360. J.W.Murray, L.S.Balistrieri, and B.Paul, Geochim. Cosmochim.Acta, 1984, **48**, 1237.
361. S.Kalhorn and S.Emerson, Geochim.Cosmochim.Acta, 1984, **48**, 897.
362. R.Jahnke, D.Heggie, S.Emerson, and V.Grundmanias, Earth Planet.Sci.Letters, 1982, **61**, 233.
363. W.S.Moore, T.L.Ku, M.D.Macdougall, V.M.Burns, R.G.Burns, J.Dymond, M.W.Lyle, and D.Z.Piper, Earth Planet.Sci.Letters, 1981, **52**, 151.
364. J.Dymond, M.Lyle, B.Finney, D.Z.Piper, K.Murphy, R.Conard, and N.Pisias, Geochim.Cosmochim.Acta, 1984, **48**, 931.
365. S.E.Calvert and D.Z.Piper, Geochim.Cosmochim. Acta, 1984, **48**, 1913.
366. Y.-H.Li, Geochim.Cosmochim.Acta, 1982, **46**, 1053.
367. J.G.Dillard, D.L.Crowther, and J.W.Murray, Geochim.Cosmochim.Acta, 1982, **46**, 755.
368. J.G.Dillard, D.L.Crowther, and S.E.Calvert, Geochim.Cosmochim.Acta, 1984, **48**, 1565.

Severtsov Institute of the
Evolutionary Animal
Morphology and Ecology,
USSR Academy of Sciences,
Moscow