Marine Chemistry, 9(1980): 49—70

PROCESSES AFFECTING PARTICULATE TRACE METALS IN THE SEA SURFACE MICROLAYER

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(Received May 1, 1979)

ABSTRACT

Hunter, K. A., 1980. Processes affecting particulate trace metals in the sea surface microlayer. Mar. Chem., 9: 49—70.

Concentrations of particulate Fe, Mn, Ni, Cu, Zn, Cd and Pb have been measured in surface microlayer and subsurface seawater samples collected in the North Sea adjacent to the East Anglian coast, in an area subject to a considerable fluvial input of clay minerals. The results are interpreted by estimating the magnitudes of different processes affecting particulate matter in the microlayer: atmospheric deposition, Brownian diffusion, gravitational settling, bubble flotation and mixing. Both Fe and Mn are strongly depleted in the microlayer, evidently as a result of gravitational settling of Fe- and Mn-bearing mineral particles out of the microlayer. These particles are mixed into the surface region from the water column beneath. Microlayer enrichment of Cu, Zn and Pb was also observed and probably results from flotation of particles attached to rising bubbles. In one set of samples, however, the marked enrichment of these elements, as well as Ni, may result instead from deposition of particles from the atmosphere directly onto the water surface.

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INTRODUCTION

A number of recent reviews (MacIntyre, 1974 a, b; Blanchard, 1975; Liss, 1975; Hunter and Liss, 1977, 1979) show an increasing awareness of the importance of exchange processes in the sea-surface microlayer. This layer is operationally defined as the upper few hundred μm of the water column (Liss, 1975). There is however a tendency to regard its behaviour as restricted to the formation of surface organic monolayers by Gibbsian adsorption at the air—sea interface. In fact, the chemistry of the microlayer region is considerably more complex than this, as is shown by the case of particulate trace metals (PTMs), which are frequently enriched in the microlayer relative to subsurface seawater (Barker and Zeitlin, 1972; Duce et al., 1972; Piotrowicz et al., 1972; Hoffman et al., 1974) and whose surface concentrations are controlled by a variety of distinct processes. Although

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considerable attention has been directed towards determining the sources of PTMs found in the microlayer (Hoffman et al., 1974; Wallace and Duce, 1975, 1978 a, b), the processes which affect particulate species within the microlayer itself have received little explicit consideration.

At least three important mechanisms capable of transporting PTMs into the microlayer are recognised. Internal water circulations, such as the helical vortex cells envisaged by Langmuir (1938), transport subsurface particulates into surface convergences (Blanchard, 1975). These convergences are frequently seen as surface streaks aligned with the wind direction (Blanchard, 1963), but little is known of the importance of this transport mechanism when the circulation is not readily seen in this way.

Hoffman et al. (1974) compared the rates of atmospheric deposition and surface microlayer concentrations of Fe, Mn and V in oceanic regions off West Africa within the Saharan dust plume, and concluded that in this area of unusually high dust concentration, the deposition rates of these metals are sufficiently high to account for the observed enrichment in the microlayer. However, in other areas of the North Atlantic, away from the dust plume, atmospheric deposition was apparently insufficient to account directly for the observed microlayer enrichment.

Wallace and Duce (1975) have estimated the flux of various PTMs to the microlayer in oceanic areas due to flotation of subsurface particulates by rising bubbles. These estimates are probably only approximate figures at best, since they are based essentially on extrapolation to the oceanic situation of laboratory measurements of particulate organic carbon (POC) flotation in coastal water and the PTM/POC composition of oceanic microplankton (Wallace and Duce, 1975). However, more recent flotation studies made directly on oceanic seawater (Wallace and Duce, 1978a) give broadly similar results. Both studies place the bubble flotation flux to the microlayer close to the rate of atmospheric deposition for a wide variety of PTMs.

Viewed in terms of the residence times of particles within the microlayer which are necessary to balance either hypothetical flux against the microlayer surface excess of PTM, these observations suggest residence times which seem very long in comparison to the likely time scales of processes mixing microlayer particulates into the subsurface water. For example, the Saharan dust plume data suggest mixing times of the order of seconds, while the POC flux from bubble flotation in oceanic waters estimated by Wallace and Duce (1975, 1978b) requires a microlayer residence time of about 10 min to account for observed enrichments of POC (Williams, 1967; Nishizawa, 1971). This is not necessarily a complication, since particles undergoing bubble flotation attach to the bubble surface as a result of interfacial tension forces (Adamson, 1976) and may therefore be considerably stabilised at the sea surface by the same mechanism. In contrast, although PTMs appear to enter the microlayer by atmospheric deposition at similar rates to bubble flotation, they may pass directly into the subsurface water if the atmospheric particles contain little or no surface-active organic matter capable of providing stabilisation on the surface.

Therefore, not only the fluxes of PTMs to the microlayer from different sources, but also the detailed processes within the microlayer region which control the residence times of PTMs in their different particulate forms must be examined. Apart from the association of PTMs with surface-active organic matter and the subsequent stabilisation of particulates at the interface, other processes must be considered, such as turbulent mixing of microlayer and subsurface waters, Brownian diffusion of particles, and gravitational settling and aggregation within the viscous sub-layer adjacent to the air—sea interface (Wallace and Duce, 1978a). Consideration of these effects has been prompted by the results of the present work, in which the concentrations of seven PTMs were measured in microlayer and subsurface samples collected in coastal waters of the North Sea. The results provide an interesting contrast with previous studies in oceanic areas and reveal, in particular, the important balance between gravitational settling and surface stabilisation of particles, which controls microlayer residence time.

EXPERIMENTAL

Sample collection and preparation

The experimental methods used in this work resemble in all essential respects those used by Piotrowicz et al. (1972) for PTMs. Sea-surface microlayer samples were collected by the Garrett (1965) screen technique, using a 55 cm-square mesh of woven nylon filaments (0.24 mm diameter) held in a frame of rigid PVC. Samples were drained into 1 dm^3 all-polythene sampling bottles previously cleaned by boiling in 50% sulphuric acid for 6—8 h followed by rinsing with double-distilled water and, in the field, excess seawater. Subsurface seawater samples were collected midway between the taking of each screen sample by opening a sample bottle ~ 20 cm below the water surface. Plastic gloves were worn throughout the sampling.

The screen delivered, on average, 55 ± 12 cm^3 of microlayer sample on each dip. This volume is equivalent to an effective sample thickness of 300 ± 66 μm spread over the void area of the mesh (~ 60%) which collects the microlayer sample. About 20 successive dips of the screen yielded 1 dm^3 of sample in approximately 30 min. Prior to each sampling trip, the screen was dismantled in the laboratory for cleaning in Decon solution, dilute HCl and double-distilled water and then sealed in a clean polythene bag for transport. In the field all sampling apparatus was thoroughly rinsed with seawater before use and the first few dips of the screen for each were rejected.

On account of the wide variability often found in microlayer composition (Barker and Zeitlin, 1972), it was decided that "replicate" samples should be taken at a relatively small number of sampling sites. Three sets of five sample pairs (microlayer + subsurface) were collected in the North Sea on 23/11/76, 6/5/77 and 13/5/77 at distances of 8, 12 and 5 km, respectively, southeast of Great Yarmouth. Table I summarises information about these sample groups, in particular the sea, wind and surface states at the time of collection. After collection the samples were transported to the laboratory for immediate filtration using oxoid cellulose membrane filters of 0.45 μm nominal pore size. Filtration was carried out in the order of sample collection, and completed in all cases within 6—7 h of the sampling time.

TABLE I

Microlayer samples collected

Sample numbers	Date collected	Distance from shore	Sea condition	Surface state
114—118	23/11/76	8 km	Calm sea Clearing fog	No visible slicks Stable bubbles especially near end of period
200—204	6/5/77	12 km	Wind Surface roughness	No visible slicks No bubbles
205—209	13/5/77	5 km	Calm surface Onshore wind	No visible slicks Many bubbles

For the first series of samples (23/11/76), the filters were frozen in clean plastic dishes to await analysis, while the other two sets were analysed immediately.

The filters were transferred to pre-cleaned 100 cm^3 Pyrex flasks and dissolved by the addition of 5 cm^3 of BDH 'Aristar' nitric acid and gentle heating for 5—10 min followed by addition of 5 cm^3 of BDH 'Aristar' perchloric acid. Each flask was then heated to just below boiling point for 30 min, and then the acid was evaporated to dryness and the residue dissolved in 10 cm^3 of 1.0 mol dm^{-3} BDH 'Aristar' HCl.

Sample analysis, blanks and precision

Analyses for Fe, Ni, Cu, Zn, Mn, Cd and Pb in the acid extracts were carried out by atomic absorption spectrophotometry (AAS) using standard flame comparison methods on a Varian 1100 instrument. Preliminary experiments verified that no substantial losses of these trace metals took place during treatment of the filters, so that working standards prepared in the HCl matrix were used for the actual AAS analyses. Procedural blanks were prepared by filtering double-distilled water and otherwise treating the filters in the same way as samples. The contribution to this blank from the acids used (HNO_3 + $HClO_4$) was also determined separately, and found to be generally the most important. The blank levels are listed in Table II for each PTM studied. The precision of the analyses determined from replicate sea-

TABLE II

Blank levels for 1 dm^3 samples

Element	Blank contribution HNO_3+HClO_4, nmol dm^{-3}	Total procedural blank, nmol dm^{-3}
Fe	130	130 (0.9–2.7%)[a]
Mn	2	4.4 (1–3%)
Ni	4	11 (10–20%)
Cu	7	8 (20–50%)
Zn	22	22 (15–40%)
Cd	1	2.8 (25–100%)
Pb	1.7	1.7 (6–20%)

[a] Values in parentheses give typical percentages of sample concentrations for each blank.

water samples was found to be: Fe and Mn, 5%, Ni, 26%; Cu, 18%; Zn, 16%; Cd and Pb, 14% (all $\pm\sigma$ limits). Similar precision was obtained by Piotrowicz et al. (1972) for particulate Fe (10%), Cu (25%), Ni (17%) and Pb (21%) using equivalent analytical techniques.

RESULTS

The complete set of results for concentrations of particulate Fe, Mn, Ni, Cu, Zn, Cd and Pb in the fifteen pairs of screen microlayer samples (*S*) and bulk or subsurface samples (*B*) is given in Table III. Also given is the microlayer enrichment factor *EF*, defined as the ratio of microlayer and bulk concentrations. Table IV shows the geometric mean of PTM concentrations for each sample group normalised with respect to Fe. Wallace et al. (1977) find particulate Fe/Al ratios to be fairly constant at values typical of the Earth's crust in coastal and most oceanic waters, indicating that in this work Fe can be taken as an indicator of the mineral content of the suspended matter.

Bulk phase PTM concentrations

The concentrations of Fe and Mn in the bulk seawater samples are uniformly higher than those of the other PTMs and are strongly correlated (correlation coefficient ρ = 0.942). Fe and Mn levels for early March 1976 are higher by a factor of about three, probably as a result of increased mixing (Head, 1971). The Mn/Fe ratios for all three sample groups vary with a standard deviation of only ~ 10% and are quite similar to the average Mn/Fe ratio for the Earth's crust, calculated on the basis of a mixture of granites and basalts by Taylor (1964). These observations point to a simple terrigenous source of particulate Fe and Mn in the suspended matter, which is not surprising considering the proximity of the sampling sites to the coast

TABLE III

Screen microlayer (*S*) and bulk seawater (*B*) PTM concentrations (nmol dm^{-3}) and microlayer enrichment factor *EF* = *S*/*B* (ratio of microlayer and bulk concentrations)

Sample	Fe	Mn	Ni	Cu	Zn	Cd	Pb
S114	13800	230	126	84	202	8.2	52
B114	18400	483	29	16	63	5.6	18
EF	0.75 ±0.06	0.48 ±0.04	4.3 ±1.6	5.3 ±1.3	3.2 ±0.7	1.5 ±0.3	2.9 ±0.5
S115	15300	370	614	45	92	5.0	28
B115	15500	356	46	11	47	5.9	15
EF	0.99 ±0.08	1.04 ±0.08	13.3 ±4.9	4.1 ±1.0	2.0 ±0.5	0.9 ±0.2	1.9 ±0.3
S116	13300	242	52	32	161	5.6	26
B116	15000	326	23	13	50	6.8	19
EF	0.89 ±0.07	0.74 ±0.06	2.3 ±0.8	2.5 ±0.6	3.2 ±0.7	0.8 ±0.2	1.3 ±0.2
S117	11500	211	46	20	69	4.0	20
B117	15300	327	127	10	65	7.9	14
EF	0.75 ±0.06	0.65 ±0.05	0.4 ±0.1	2.0 ±0.5	1.1 ±0.2	0.5 ±0.1	1.4 ±0.2
S118	12800	207	263	12	34	8.1	18
B118	15000	315	33	4	33	19.6	15
EF	0.85 ±0.07	0.66 ±0.05	8.0 ±2.9	3.0 ±0.8	1.0 ±0.2	0.4 ±0.1	1.2 ±0.2
S200	2930	78	23	23	68	1.4	17
B200	4610	110	20	12	42	<0.5	3
EF	0.64 ±0.05	0.71 ±0.05	1.2 ±0.4	1.9 ±0.5	1.6 ±0.4	>1	2.1 ±0.4
S201	4410	112	17	16	130	7.9	8
B201	3530	93	20	17	132	1.1	5
EF	1.25 ±0.10	1.20 ±0.09	0.9 ±0.3	0.9 ±0.2	1 ±0.2	7 ±1.4	1.3 ±0.2
S202	3340	87	16	42	58	1.1	12
B202	5220	115	13	16	36	1.1	6
EF	0.64 ±0.05	0.76 ±0.06	1.2 ±0.4	2.6 ±0.7	1.6 ±0.4	1 ±0.2	2 ±0.3
S203	5370	118	33	84	177	2.3	34
B203	5190	138	48	25	128	1.1	10
EF	1.03 ±0.08	0.86 ±0.07	0.7 ±0.3	3.4 ±0.9	1.4 ±0.3	2 ±0.4	3.4 ±0.6
S204	2800	54	24	14	66	<0.5	15
B204	3360	89	19	14	45	1.1	10
EF	0.83 ±0.06	0.61 ±0.05	1.3 ±0.5	1.0 ±0.3	1.5 ±0.3	<1	1.5 ±0.3
S205	4540	80	12	8	34	<0.5	13
B205	5560	116	12	6	24	<0.5	5
EF	0.82 ±0.06	0.69 ±0.05	1 ±0.4	1.3 ±0.3	1.4 ±0.3		2.6 ±0.4
S206	4430	85	<6	7	41	1.9	7
B206	7710	199	17	7	31	1.8	10
EF	0.57 ±0.04	0.43 ±0.03	<1	1.0 ±0.3	1.3 ±0.2	1.1 ±0.2	0.7 ±0.1
S207	4590	86	<6	11	31	<0.5	8
B207	6770	160	<6	4	29	<0.5	5
EF	0.68 ±0.05	0.54 ±0.04		2.8 ±0.7	1.1 ±0.2		1.2 ±0.2
S208	7130	165	<6	8	30	<0.5	7
B208	6840	155	12	4	29	<0.5	6
EF	1.04 ±0.08	1.06 ±0.08	<1	2.0 ±0.5	1.0 ±0.2		1.2 ±0.2
S209	5150	93	<6	7	31	<0.5	9
B209	6170	134	<6	6	53	<0.5	8
EF	0.83 ±0.06	0.69 ±0.05		1.2 ±0.3	0.6 ±0.1		1.1 ±0.2

TABLE IV

Geometric mean PTM concentrations normalised with respect to iron (10^3 mol/mol)

Sample group	Mn/Fe	Ni/Fe	Cu/Fe	Zn/Fe	Cd/Fe	Pb/Fe
Bulk samples						
B114—118	22.6	2.65	0.62	3.18	0.51	1.02
B200—204	25.0	5.02	3.78	11.35	0.22	1.81
B205—209	22.9	1.48	0.80	4.86	0.10	1.00
Screen samples						
S114—118	18.5	10.33	2.34	7.02	0.45	2.01
S200—204	23.7	5.91	7.76	18.45	0.47	4.18
S205—209	19.3	1.4	1.59	6.53	0.14	1.68
Average crust (Taylor, 1964)	16.6	1.26	0.86	1.06	0.0018	0.06
Average coastal sediments (Chester, 1965)	—	4.3	1.7	—	—	0.26
Microplankton (Martin and Knauer, 1973)	8.0	6.0	29.3	398	0.43	4.49

and the Breydon Water estuary. These two PTMs probably occur as hydrous oxides in association with river-borne terrigenous clay minerals. Zaim (1977) has found that the suspended matter in this area of the North Sea is dominated by clay minerals such as montmorillonite, kaolinite and illite, as well as variable amounts of quartz.

The five other PTMs are not significantly correlated with either Fe or Mn, although Ni and Cu show PTM/Fe ratios which are similar to or slightly higher than values typical of the average for the Earth's crust or "average" coastal sediments (Table IV). PTM/Fe ratios for Zn, Cd and Pb are appreciably higher than crustal values, suggesting that these PTMs come largely from a source other than simple crustal weathering. The highest PTM/Fe ratios for all elements except Cd occur in the sample set (200—204) which was collected furthest from shore. This may indicate a decreasing influence of terrigenous minerals as carrier phases for PTMs as distance from the coast increases.

Microlayer PTM concentrations

A clear and unusual feature of the microlayer results in Table III is the depletion of both Fe and Mn in most of the microlayer samples. Only samples S115, 203 and 208 have the same concentrations as their respective bulk seawater samples and S201 is the only one which shows a slight enrichment. The depletion of Fe and Mn in the remaining majority of samples is maintained in spite of the seasonal change in bulk PTM levels and the differences in distance from the coast, suggesting that at least in this part of the North Sea, depletion of Fe and Mn (and presumably the alumino-silicate minerals with which they appear to be associated) is a general and relatively constant phenomenon. The Mn/Fe ratios (Table IV) indicate that the behaviour of the two elements is not entirely similar, although microlayer concentrations are still significantly correlated ($\rho = 0.88$). For the two sites nearer the coast (114—118, 205—209), the Mn/Fe ratios are nearer to that for average crust than to those for the corresponding bulk samples, while for the more distant site (200—204) the Mn/Fe ratios in the microlayer and bulk water are similar.

Of the other 5 PTMs, only Cd shows any evidence of the depletion observed so consistently for Fe and Mn. For the early winter 1976 samples, two or three microlayer samples are apparently depleted in Cd, while the Cd concentrations in the other two sample sets are too low for any reliable deduction to be made. The other PTMs, in the 1976 microlayer samples, Ni, Cu, Zn and Pb all seem to be generally enriched, with a few exceptions. This sample set shows an interesting trend, best illustrated by the results for Cu and Pb, for which microlayer PTM concentrations steadily decrease with the order of sample collection from 114 to 118. The trend is not consistent for Ni and Zn, but the concentrations of these two PTMs in the earliest collected microlayer samples tend to be higher than in those taken later.

This set of samples was collected during clearing fog with stable bubbles at the water surface (Table I). These conditions are ideal for the formation of surface slicks because of the absence of wind. Under normal conditions, wind tends to sweep the water surface clean, producing foam patches and stable bubbles (Baier, 1972). No compressed surface slicks were present in the immediate sampling area, but numerous slick-covered regions were observed while motoring into the area before sampling began. The microlayer enrichments of Ni, Pb, Cu, and Zn in this set of samples may result from deposition of fog-scavenged particles from the atmosphere, as discussed later.

Wind speeds were higher during collection of the two late spring 1977 sets of samples. No surface slicks were seen, but stable surface bubbles were present during collection of the second set (205—209). The consistent decrease in microlayer PTM concentrations with the order of sampling is also absent. Although bulk seawater levels of Ni, Cu and Zn are similar to, or slightly smaller than, those seen in the early winter 1976 set, only Cu and Pb show any consistent evidence for enrichment in the later samples. There is no convincing evidence for microlayer enrichment of Ni, in contrast to the earlier results where Ni is generally the most enriched. In the final group (205—209), Ni concentrations in both bulk seawater and the microlayer are quite low. For Cu, Pb and, to a lesser extent, Zn, the pattern of enrichment results seen in the earlier samples is preserved, but enrichment factors are considerably reduced.

The PTM/Fe ratios for the microlayer samples (Table IV), especially for the first two sample sets, are uniformly higher than the crustal values for all PTMs other than Mn and possibly Cd. A pure aluminosilicate source for the suspended PTM matter found in the microlayer is, therefore, unlikely. This suggests that other phases such as detrital organic matter and/or organically-stabilised colloidal aggregates exercise an important control over the levels of Ni, Cu, Zn and Pb in microlayer particulate matter (Wallace et al., 1977). Table IV shows PTM/Fe ratios for marine microplankton calculated from the data of Martin and Knauer (1973). Microplankton have been assumed to have a PTM composition typical of particulate organic phases subject to flotation by rising bubbles (Wallace and Duce, 1975; Wallace et al., 1977). These ratios are similar to, or greater than, PTM/Fe ratios in microlayer samples for Ni, Cu, Zn, Cd and Pb. Since most of the Fe in these samples is associated with terrigenous materials, organic detritus with a PTM composition similar to that of microplankton will give lower PTM/Fe ratios when diluted with a major Fe-bearing phase. Thus the present data are at least consistent with an important organic-rich phase for Ni, Cu, Zn, Cd and Pb, which adds little to the overall levels of Fe and Mn. As a result of this, the enrichment of trace metals such as Cu, Zn and Pb and the depletion of Fe and Mn may be a result of enrichment in the microlayer of surface-active organic phases, relative to minerals of essentially crustal composition, which are not stabilised at the surface to the same extent.

The behaviour of the seven PTMs studied in coastal North Sea waters may be conveniently summarised as follows:

(a) Both Fe and Mn are closely related and are consistently depleted in the microlayer. Near to the coast, Mn appears more depleted than Fe, but 12 km offshore the differences between the two elements are small.

(b) Cu, Zn and Pb are consistently enriched in the microlayer and appear not to be controlled exclusively by the Fe- and Mn-bearing phases, especially further from the coast.

(c) There is no convincing evidence for Cd enrichment in the microlayer. In the early winter 1976 samples where Cd concentrations are highest, this element appears to follow the depletion of Fe and Mn. ([illegible])

(d) Ni was not normally enriched in the microlayer in late spring 1977, but was highly enriched in the unusual set of samples collected in early winter 1976 during clearing fog.

The different behaviours of the seven PTMs can be substantially confirmed by principal components analysis of the late spring 1977 data (the set 114—118 was omitted because of the unusual behaviour of Ni). Three eigenvectors were obtained which together accounted for 95.7% of the sample variance, as follows:

0.49Ni + 0.49Cu + 0.51Zn + 0.51Pb	52.5% of sample variance
0.68Fe + 0.69Mn	28.0% of sample variance
0.95Cd	15.2% of sample variance

(eigenvector coefficients less than 0.17 have been omitted for the sake of clarity).

DISCUSSION

The consistent depletion of Fe and Mn observed in the North Sea contrasts with the results of earlier workers. Piotrowicz et al. (1972) found particulate Fe to be markedly enriched in screen samples collected in Narragansett Bay (Rhode Island), with a geometric mean *EF* of 2.6 for 8 samples. In New York Bight, Fe was also clearly enriched (*EF* ~1.8 for 5 samples), while particulate Mn showed no strong evidence for enrichment (*EF* ~ 0.9 ± 0.4). In oceanic waters, Hoffman et al. (1974) found consistent evidence for enrichment of Fe, Mn and V in the microlayer, even far from the influence of the Saharan dust plume within which atmospheric deposition is the principal cause of microlayer enrichment.

Depletion of particulate species has not frequently been observed in microlayer samples, most published data being restricted to biological species. Indeed, enrichment of dissolved and particulate materials is so commonly observed that it has almost become a sine qua non of microlayer research (see, however, Chapman and Liss, 1979). Harvey's (1966) results for diatoms in microlayer samples collected by a rotating ceramic drum device show frequent surface depletion. Sieburth et al. (1976) found depletion of cultivable bacteria and amoebae in one microlayer sample in the North Atlantic caused, apparently, by growth inhibition as a result of substances released to the microlayer by a bloom of *Nitzschia*.

The contrast in behaviour between Fe and Mn, both of which are consistently depleted in the microlayer, and the other PTMs that show frequent enrichment, indicates that there are at least two important phases containing trace metals in the particulate matter, each of which behaves differently in the microlayer. The first phase, which bears most of the Fe and Mn, probably consists of river-derived terrigenous minerals and aggregates of relatively large particle size. The depletion of this phase and its associated trace metals in the microlayer is thought to arise from rapid sedimentation of these large particles out of the microlayer region. In contrast, the other PTMs are largely carried by a second type of phase or phases, which give rise to frequent enrichment in the microlayer, and are believed to consist of organically-bound aggregates of colloidal minerals and/or organic detritus, both of relatively small particle size. The enrichment of these phases and their associated trace metals is more complex and can arise from a combination of bubble flotation, atmospheric deposition and sedimentation out of the microlayer. For this group, stable attachment of particles at the air—sea interface by means of interfacial forces is of central importance and will be shown to be associated with the presence of organic matter in the particulate material.

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The second group of PTMs (Ni, Cu, Zn, Cd, Pb) is present in microlayer particulate material at levels which are substantially higher than the typical crustal abundance. Thus the microlayer depletion of their terrigenous component, which must occur along with that of Fe and Mn, should be minor in comparison with the effects produced by the more important phases controlling these elements. Conversely, the enrichment of that component of particulate Fe and Mn carried by the microlayer-enriched phases is small relative to the depletion of the major, terrigenous phase.

The remainder of this paper is concerned with a detailed explanation of the present results in terms of the different processes occurring in the microlayer, which act as sources of PTMs and control their residence times there. Since no explicit consideration of this important subject has appeared in the literature, an opportunity is taken here to describe briefly the principles underlining particulate exchange in the microlayer and to review the results of previous studies.

Processes affecting particles in the surface microlayer

The principal processes which influence PTM concentrations in the microlayer region are illustrated schematically in Fig.1. Deposition of atmospheric particles onto the sea surface and flotation of surface-active particulates by rising bubbles both act as direct sources of microlayer particles which can cause surface enrichment. Under special circumstances, regular internal water

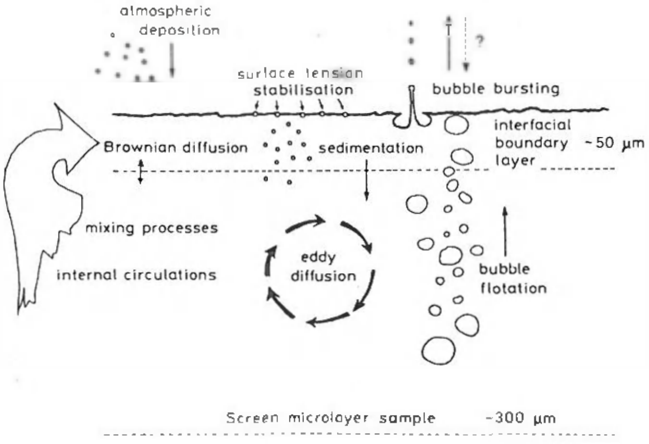

Fig.1. Transport processes for particulate matter in the microlayer. The screen microlayer sample (~300 µm) is divided into an upper hydrodynamic boundary layer (~50 µm) within which turbulence is damped, and a lower region which behaves like subsurface water and is well mixed by eddy diffusion. Diagram not entirely to scale — actual oceanic bubbles have a similar size to the whole microlayer region and must introduce substantial mixing as they break through the boundary layer. This is incorporated in "mixing processes"

circulation as envisaged by Langmuir (1938) can also transport particulate matter into surface convergences or windrows (Blanchard, 1975).

At least three distinct processes contribute to the removal of particles from the microlayer region. Gravitational settling within the microlayer is expected to be especially important for relatively large, dense particulate matter. Transit times during settling will depend both on settling velocities and, for particles attached to the air—sea interface, on the stabilising forces provided by interfacial tensions. Brownian diffusion, which is most rapid for very small particles, will tend to move particles along the concentration gradient established by other processes, thus acting as a removal mechanism for enriched microlayers and vice versa. The "u"-shaped dependence of removal rate on particle size for both Brownian diffusion and gravitational settling is analogous to that which occurs in dry deposition processes in the atmosphere (Hunter and Liss, 1977; Slinn et al., 1978). Finally, regions or parcels of water at the surface will be replaced by subsurface water as a result of turbulent mixing processes resulting from wave breaking, bubble bursting and internal circulation waves.

Vertical eddy diffusion, which maintains essentially complete mixing in the water column immediately beneath the microlayer, will be considerably damped in the interfacial boundary layer for turbulence adjacent to the air—sea interface. Kanwisher (1963) has remarked on the stability of particles in this layer when the surface is subject to horizontal shear due to wave action. For the exchange of dissolved gases across the air—sea interface, the thickness of the interfacial boundary layer is about 50 μm, depending on surface wind velocity and turbulent effects (Peng et al., 1979), i.e. about a factor of six smaller than the thickness of the screen microlayer sampled in this work.

(a) Sedimentation

The data of Hoffman et al. (1974) in areas within the Saharan dust plume indicate that for wind velocities in the range 5—10 m s^{-1}, the residence time of particulate Fe, Mn and V deposited from the atmosphere in a 300 μm-thick surface microlayer is of the order of 2 s. In the absence of mixing by Brownian diffusion, and of turbulent replacement of the surface film region, particles which sediment in the water column at velocities below that of dry deposition from the atmosphere (1—6 cm s^{-1} for the Saharan aerosol (Sehmel and Sutter, 1974), taken as 3 cm s^{-1} by Hoffman et al. (1974)) would accumulate in the surface boundary layer. Data given by Junge (1972) suggest that the major mass of particles in the Saharan dust is in the range 4—8 μm diameter, equivalent to a spherical-particle Stokes settling velocity in the range 12—48 μm s^{-1}. Particles settling within this velocity range in the water column would traverse a 50 μm-thick boundary layer for eddy diffusion inside the microlayer in just a few seconds at most. This time is comparable to the apparent residence time calculated from the atmospheric deposition rate. Thus the major removal mechanism of soil-sized dust particles appears to be gravitational sedimentation. Particles of colloidal size, on the other hand (e.g., 0.2—0.4 μm diameter) will have residence times of the order of 10 min with respect to removal by this mechanism.

(b) Brownian diffusion

Simple calculations indicate that Brownian motion of particles is relatively unimportant in determining microlayer residence time. The exchange flux due to this process in the interfacial boundary layer of thickness $\delta \sim 50\ \mu$m is given by

$$F_B = -D(\partial C/\partial x) \simeq -(D/\delta)(C_\mu - C_b)$$

where C_μ and C_b are microlayer and subsurface PTM concentrations respectively. The effective diffusion coefficient D for a spherical particle of radius r is (Einstein, 1926)

$$D = RT/6\pi N_A\ \eta r$$

where η is the fluid viscosity, N_A is the Avogadro number and R, T have their usual meanings. The flux due to Brownian motion (F_B) will replace the surface excess of PTM in the microlayer $(C_\mu - C_b)d$, where d is the microlayer thickness of 300 μm, on a time scale equal to

$$t_B = (C_\mu - C_b)\,d/F = N_A\ \pi\eta d^2 \cdot r/(RT)$$

where $d \sim 6\delta$. Substitution of the appropriate value for N_A, and with $RT \sim 2.4 \times 10^3$ at 20°C, $d \sim 300\ \mu$m and $\eta = 1.08 \times 10^{-3}$ kg m^{-1} s^{-1} for seawater (Riley and Skirrow, 1975), leads to the numerical result

$$(t_B/s) = 7.5 \times 10^{10}\ (r/m)$$

Thus, even particles as small as 1 nm radius should have exchange times for Brownian diffusion of the order of several minutes, while particles in the Saharan dust aerosol (2—4 μm radius; Junge, 1972) will exchange by this mechanism alone within time scales of the order of 2—4 days.

(c) Mixing processes

The fact that substantial microlayer enrichment of particulate Fe, Mn and V is observed within the area of the Saharan dust plume indicates that processes mixing subsurface water into the surface boundary layer with winds of 5—10 m s^{-1} are intrinsically slower than the vertical transfer by gravity of particles into and out of this region (Hoffman et al., 1974). The present situation in the coastal North Sea differs from that in the Saharan dust plume in one subtle respect: the source of relatively large particles containing Fe and Mn is the water column beneath the microlayer, so that Fe- and Mn-bearing particulates are brought into the microlayer by turbulent mixing of subsurface water with the surface boundary layer, and are then removed by gravitational settling. Thus, since mixing of subsurface water into the microlayer is intrinsically slower than sedimentation of relatively large soil-sized particles, the hydrodynamic surface boundary layer must become depleted in particulate material. This accounts for the depletion of Fe and Mn observed in the North Sea.

By making the (unsupported) assumption that the mixing processes are roughly negligible in comparison to sedimentation times, i.e. that the surface boundary layer within the microlayer is completely devoid of particulate Fe and Mn, an estimate can be made of the thickness (δ) of this boundary layer. The microlayer concentration C_μ is now given by

$$C_\mu = [(d - \delta)/d]\, C_b$$

giving

$$EF = C_\mu / C_b = (d - \delta)/d$$

Taking $d = 300\ \mu m$ for the microlayer thickness, as before, and a typical EF value of 0.76 (geometric mean of results in Table III) gives δ as 72 μm, which compares closely with boundary layer thicknesses for the exchange of gases (~ 50μm, Peng et al., 1979).

Mathematically, the balance between turbulent mixing processes and sedimentation may be described by a simple box model where the rate of change of microlayer concentration C_μ is given by

$$dC_\mu/dt = k_1 C_b - k_1 C_\mu - (\nu/\delta)\, C_\mu$$

Here, k_1 is the rate constant for mixing and ν is the sedimentation velocity of particles. At steady state

$$k_1 C_b = k_1 C_\mu + (\nu/\delta)\, C_\mu$$

hence

$$EF = C_\mu / C_b = k_1 / [k_1 + (\nu/\delta)]$$

Thus when the sedimentation rate (ν/δ) exceeds k_1, the rate of mixing (as in the case of Fe and Mn in the present work), the microlayer is depleted in particulate Fe and Mn relative to subsurface water. Conversely, if the mixing rate exceeds sedimentation then $EF \sim 1$. This is likely to be the case for the other PTMs studied, since if they are associated with relatively small particulates, their residence times with respect to sedimentation will be relatively long. To account for the observed enrichments of these PTMs, it is therefore necessary to consider both a mechanism for retention of particles at the interface (surface stabilisation), and also fluxes which direct particles to this region (bubble flotation, atmospheric deposition).

(d) Surface stabilisation of particles by interfacial forces

Simple calculations (e.g., Adamson, 1976) suggest that this stabilisation can be considerable in favourable circumstances. Fig.2 depicts schematically the attachment of a spherical solid particle of radius r to the sea surface

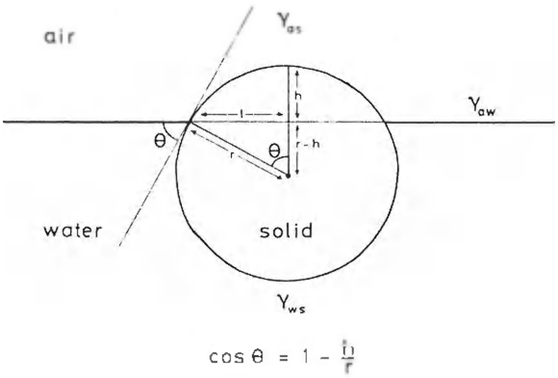

Fig.2. Equilibrium attachment of a spherical solid particle to the air—water interface.

(assumed to be flat for the sake of simplicity). For a change dh in the height of the particle cap above the sea surface, the changes in the areas of the air/solid (A_{as}), water/solid (A_{ws}) and the air/water (A_{aw}) interfaces are given by, respectively, $dA_{as} = -dA_{ws} = 2\pi rh$ and $dA_{aw} = -2\pi(r - h)\, dh$. The accompanying changes in the Gibbs free energy of the system are then given by

$$dG = -\gamma_{as} 2\pi r dh + \gamma_{ws} 2\pi r dh + \gamma_{aw}\, 2\pi(r - h)\, dh$$

where γ_{as}, γ_{ws} and γ_{aw} are the interfacial tensions of the air/solid, water/solid and air/water interfaces respectively. Setting $dG = 0$ for the equilibrium state and simplifying, we obtain the expression

$$\gamma_{as} = \gamma_{ws} + \gamma_{aw} \cos\theta$$

which has the same form as Young's equation for the wettability of solid surfaces by liquids (Zisman, 1964). Inspection of Fig.2 shows that θ is the contact angle between the solid and liquid phases in the presence of air. It follows that if the solid surface is not wetted by seawater ($0 < \theta < \pi$), the thermodynamically stable position of the solid particle is in the air—seawater interface, whereas if the solid is seawater-wetted, $\theta = 0$ and the particle is more stable in the aqueous phase. The important point in this respect is that most mineral surfaces likely to be encountered in seawater, e.g. clays, metal oxides and carbonates, have relatively high values of surface energy $\gamma_{as} - \gamma_{ws}$ and are, therefore, readily wettable.

However, many high-energy surfaces placed in seawater adsorb natural organic surfactants from solution (Neihof and Loeb, 1972, 1974; Loeb and Neihof, 1975; Hunter, 1977, 1979), giving rise to highly oxygenated organic films with lower surface energies. In mineral flotation, surface coverages by organic surfactants as low as 5% can give rise to contact angles of 50—70° and successful bubble flotation of particles much larger than those normally encountered in seawater (Davies and Rideal, 1963). The restoring force resisting displacement of a particle attached to the surface as in Fig.1 can be very substantial, depending on the value of θ, i.e. the surface free energy G where

$$G = \pi l^2 \gamma_{aw} = \pi r^2 \sin^2 \theta \gamma_{aw}$$

For a highly oxygenated organic surface of typical free energy 30×10^{-3} N m^{-1} (Zisman, 1964), F_r is the order 7.5×10^{-5} N for a 4-μm particle, i.e. at least 10^5 times its likely weight. For surface energies nearer the air—water interfacial tension (50—70×10^{-3} N m^{-1}, depending on the presence of surface films), θ becomes very small and attachment is much less stable.

The effect of this stabilising influence on particles resting in the interface in the presence of turbulent disruptive forces is difficult to quantify, but it is clear that organic-rich particles of low surface energy should have their residence times in the microlayer appreciably enhanced by this mechanism.

(e) Atmospheric deposition

Cambray et al. (1975) have measured the rates of atmospheric deposition of a large number of PTMs into two coastal regions of the North Sea adjacent to the sampling area: Gresham (Norfolk) and Leiston (Suffolk). The mean deposition rate for these two sites, taken from their data, is given in Table V for all of the PTMs studied (except Cd). For the latter element,

TABLE V

PTM flux calculations for coastal North Sea surface microlayer

Quantity	Fe	Mn	Ni	Cu	Zn	Cd	Pb
Geometric mean bulk concentration 1977, nmol dm^{-3}	5320	127	15	8.9	46	0.9	6.2
Atmospheric deposition rate[a], 10^{-12} mol m^{-2} s^{-1}	55	1.2	1.7	<2	3.9	0.003	1.3
Residence time t_{atm} for EF=2, min	484	529	44	>22	59	1500	24
Bubble flotation rate[b], 10^{-12} mol m^{-2} s^{-1}	470	3.8	2.7	14	180	0.2	2.1
Residence time t_{flot} for EF=2, min	57	167	28	3.2	1.3	23	15

[a] Atmospheric deposition rates are means of data given by Cambray et al. (1975) for Gresham in Norfolk and Leiston in Suffolk. Value for Cd taken from Wallace and Duce (1975) for Bermuda.

[b] 100 times bubble flotation flux calculated by Wallace and Duce (1975) for oceanic water.

the deposition rate at Bermuda given by Wallace and Duce (1975) is used, since no Cd data were given by Cambray et al. (1975). Also given are the geometric mean PTM concentrations found in the 1977 subsurface water samples taken from Table III.

The residence time necessary to give rise to a microlayer enrichment $EF = 2$, as a result of the atmospheric deposition alone, was calculated for each PTM as

$$t_{\mathrm{atm}} = (C_{\mu} - C_{\mathrm{b}})\, d/F_{\mathrm{atm}}$$

The results obtained are also given in Table V. The values found for Fe and Mn (of the order of 500 min) are too long, relative to the residence times associated with gravitational settling for the majority of mineral particles, to have any adverse effect on the microlayer depletion, even if the particles depositing on the surface contain sufficient surface-active material to stabilise them at the interface. A comparison of observed microlayer enrichments of POC with the bubble-induced flux of POC to the ocean surface (estimated by Wallace and Duce, 1975) suggests that the likely residence time of particles stabilised at the sea surface by this mechanism is an order of magnitude lower. The indicated residence time for Cd is also very long, although this may have arisen because of the use of the Bermuda deposition figure which may be too low for the coastal North Sea. Nevertheless, Cd is the PTM which most closely resembles Fe and Mn in its microlayer behaviour.

Residence times for Ni, Cu, Zn and Pb are appreciably lower than those for Fe, Mn and Cd and, considering the likely margin of uncertainty in predicting the true behaviour of the microlayer, are reasonably close to the 10 min value adopted above. This suggests that atmospheric deposition may be an important source of microlayer PTMs, if depositing particles contain sufficient organic material for stabilisation at the interface.

(f) Bubble flotation

From flotation rates for POC in Narragansett Bay water in a laboratory foam tower, Wallace and Duce (1975) estimated a value of 4.4 μg m^{-2} s^{-1} for the bubble flotation flux of POC in coastal waters (POC ~ 300 μg dm^{-3}).

For this work, estimates of the bubble flotation rates of different PTMs in coastal waters of the North Sea were obtained from this flux of POC, by assuming the PTM/POC ratios of marine microplankton (Martin and Knauer, 1973) to be typical of organic detrital matter capable of bubble flotation (Wallace and Duce, 1975). The bubble flotation fluxes for coastal water obtained in this way are given in Table V together with t_{flot}, the microlayer residence time needed to account for a microlayer enrichment of $EF = 2$ by means of the bubble flux alone.

It must be stressed that such a calculation is only a crude approximation of the true bubble-induced flux of PTM to the microlayer, which must vary considerably with surface conditions (wind, wave action and bubble

TABLE VI

Required microlayer residence times for *EF* = 2 from bubble flotation (minutes)

PTM	North Sea (present work)	Narragansett Bay[a]	New York Bight[a]	North Atlantic
Fe	57—168	2.0	8.7	18[b]
Mn	167—470	—	61	15[b]
Ni	28—78	18	—	—
Cu	3.2—3.6	1.1	1.1	12[c]
Pb	15—38	4.2	3.9	26[c]
Zn	1.3—1.4	—	—	—
Cd	20—23	—	—	—

[a] Narragansett Bay and New York Bight data from Piotrowicz et al. (1972). [b] North Atlantic data from Hoffman et al. (1974) — original oceanic bubble flotation flux of Wallace and Duce (1975) used. [c] Data from Piotrowicz et al. (1972).

concentrations). Little can therefore be said of the absolute magnitude of the residence times obtained. However, POC fluxes calculated by the same method indicate that microlayer residence times of the order of 10 min will account for the observed results (Wallace and Duce, 1975, 1978b). Since the residence times calculated for Fe and Mn are considerably in excess of this value, it seems fair to conclude that the fluxes of Fe and Mn introduced to the microlayer by flotation are too low to have a measurable effect on surface concentrations in the North Sea (in particular, the depletion caused by sedimentation). In contrast, the residence times for the other PTMs are all of the same order as that assumed for POC, suggesting that these elements ought to be enriched in the microlayer, as was frequently found. Indeed, the three elements which show the most consistent enrichment in the 1977 set of samples, Cu, Zn and Pb, have the lowest residence times predicted by the model. Table VI gives the values of t_{flot} for the 1976 and 1977 sets of samples, together with similar values calculated (using the same PTM fluxes) for Narragansett Bay and New York Bight. For the latter, bulk PTM concentrations were taken from Piotrowicz et al. (1972). In addition, oceanic values were calculated using the original PTM fluxes of Wallace and Duce (1975) and bulk PTM data for Fe and Mn from Hoffman et al. (1974) and for Cu and Pb from Piotrowicz et al. (1972). Most of these residence times are in the range found for the North Sea PTMs other than Fe and Mn, again consistent with the observation of microlayer enrichment in the studies cited. One notable exception is Mn in New York Bight, which has an appreciable predicted residence time (61 min), consistent with the lack of Mn enrichment found by Piotrowicz et al. (1972) in this area.

An important difference between the North Sea results and those of earlier work emerges from these calculations. The residence times for Fe in the three other areas of study, and for Mn in the North Atlantic, are low enough to be consistent with the enrichments observed in each case. The much higher residence times of Fe and Mn in the present study arise from the same model calculations as a result of the considerably higher bulk concentrations of these elements. In other words, the apparently non-surface-active Fe- and Mn-bearing phases are relatively less abundant in the earlier studies, so that the enrichment of Fe and Mn phases as a result of the component subject to bubble flotation is not swamped by depletion, as it is in the area of the present work.

Comparison of bubble flotation and atmospheric deposition for the North Sea

Estimates of bubble flotation PTM flux to the microlayer are consistently higher than measured rates of atmospheric PTM deposition for Fe, Cu, Zn and Cd, and are very similar for Mn, Ni and Pb. This differs from the situation predicted for oceanic areas (Wallace and Duce, 1975, 1978a), where the two rates are comparable for most elements. Under conditions of calm sea and low wind, atmospheric deposition in oceanic areas is expected to compete effectively with bubble flotation as a source of microlayer PTM (Wallace and Duce, 1978a). The corresponding situation in coastal North Sea waters should be, according to the flux data in Table V, an increasing contribution of Ni and Pb (which have the lowest value of t_{atm}) to microlayer PTM content, relative to Cu and Zn, which have the lowest values of t_{flot} and may therefore result largely from bubble flotation.

It can be seen from Table III that the 1976 samples collected under calm conditions during clearing fog conform essentially to this picture. The enrichment of Ni is the highest of this group although this element is not significantly enriched in the 1977 samples. This observation, coupled with the unusual decline in microlayer PTM concentrations with time as the fog cleared, suggests that atmospheric deposition may be a major source of microlayer PTMs. Indeed, atmospheric deposition in this case may have been appreciably accelerated by fog scavenging of suspended particles.

CONCLUSIONS

This work illustrates the variety of processes which control the concentration of particulate species in the microlayer. A number of further investigations will be necessary in order to understand these processes and their relative importance in different environments more fully. For the coastal North Sea and other areas subject to a major input of terrigenous mineral material, it would be of interest to investigate microlayer enrichment of particulate Fe and Mn, as well as Al, Si and other mineral indicators, as a function of increasing distance from the coast. As the terrigenous input of rapidly-settling particles decreases in relation to PTMs bound up by surface-active phases such as organic detritus, the depletion observed in the present study should revert to enrichment. Other refinements such as more reliable estimates of bubble flotation fluxes of PTM, measurement of the settling rate of Fe- and Mn-bearing particulate matter and the partition of these elements into surface oxide coatings, matrix Fe and Mn, organic Fe and Mn, etc., would be of interest.

A major unknown in this area of microlayer chemistry remains, however, the residence time appropriate to dry or wettable particles, and to particles made stable at the interface by surface tension. The results and discussion given have indicated that the best estimates we can make at the present time are $t_{res} \sim 2$ s for wettable material of either atmospheric or terrigenous origin, and $t_{res} \sim$ 1—30 min for surface-stabilised particles. These values are consistent with all of the available field evidence and illustrate, if nothing else, the magnitude of the stabilisation afforded to particles resting at the interface by interfacial forces. This stabilisation, amounting to an increase of between 30 and 900 times in residence time does not seem surprising, in view of the magnitude (suggested by simple calculation) of the forces restraining particles in the surface.

ACKNOWLEDGEMENTS

I am indebted to P.S. Liss for his guidance and encouragement during the period in which this work was carried out, as well as to P. Brimblecombe, R. Chesselet and P. Buat-Ménard for helpful discussions and advice leading to the preparation of the manuscript. T. Adams and L. Cartwright provided invaluable assistance with the sample collection. This work was carried out when the author was in receipt of a Rutherford Scholarship from the Royal Society, London which is also thanked for subsequent support in the form of a European Exchange Fellowship. Additional support from the New Zealand University Grants Committee is gratefully acknowledged.

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