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Positively charged suspended particles: Studies in an iron-rich river and its estuary[1]

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Abstract

Natural particles in suspension in fresh, marine, and estuarine surface waters generally display a narrow range of negative electrophoretic mobilities. The measured mobilities are thought to be controlled by organic and oxide surface coatings, and there is considerable evidence for control by the organic coatings. Here we present results which indicate that oxide-hydroxide coatings can control the mobility under conditions found in a river fed by acid-mine drainage, but that organic coatings, when present, assume overall mobility control. Electrophoretic measurements show positively charged river particles acquiring less positive and then negative charges in estuarine waters. In the river and at low salinities mobility is affected by the pH of the water. At higher salinities the oxide-hydroxide character is less evident, and particles assume the negative mobilities normally found in natural waters and attributed to organic surface coatings.

Suspended particles in a wide variety of fresh, marine, and estuarine surface waters have been found to exhibit only negative electrophoretic mobilities (Neihof and Loeb 1972, 1974; Hunter and Liss 1979, 1982; Tipping et al. 1981; Loder and Liss 1982, 1985; Hunter 1983). Mean mobilities (U_E) fall in the range -0.7 to -2.0×10^{-8} m^2 s^{-1}V^{-1}, despite the wide variety of particles that usually comprise the suspended particulate load (e.g. clays, oxides, carbonates, plankton, organic debris, and biological detritus). This range of particle types might be expected to show a wide spread of negative and positive mobilities in natural waters (Brinton and Lauffer 1959; Parks and de Bruyn 1962; Parks 1975; Stumm and Morgan 1981). The apparent uniformity indicated by the narrow mobility range has been attributed to the presence of organic or oxide surface coatings, interacting with divalent cations such as Ca^{2+} and Mg^{2+} (Neihof and Loeb 1972, 1974; Hunter and Liss 1979, 1982; Hunter 1980; Tipping 1981; Loder and Liss 1982). Thus, electrophoretic mobility measurements both present an insight into the electrical charge environment at the particle–water interface and indicate surface coatings to be ubiquitous on natural suspended particles. Such coatings can modify many of the chemical and physical processes operating on the particles, such as adsorption, desorption, precipitation, dissolution, aggregation, and disaggregation (Davis and Leckie 1978; Balistrieri et al. 1981; Baccini et al. 1982; Lion et al. 1982; Tipping and Cooke 1982; Tipping and Higgins 1982; Gibbs 1983; Tipping and Ohnstad 1984; Nyffeler et al. 1984; Eisma 1986).

Recent studies on an iron-rich river and estuary (Keithing Burn, Inverkeithing, Scotland) suggest that oxide-hydroxide phases may influence mobility when there is insufficient organic material to fully coat particle surfaces, but that overall mobility control is by organic coatings (Loder and Liss 1982, 1985). However, this conclusion is inferential, there being no evidence of oxide-hydroxide coatings influencing the mobility of particles in situ.

Here we present further work on Keithing Burn and a study of the Carnon River (Cornwall, U.K.) which is fed by highly acidic, iron-rich mine drainages. Large amounts of new oxide-hydroxide surface are continuously precipitated in the Carnon River. Particle electrophoresis is used to assess factors controlling mobility in both the river and estuary.

We thank G. E. Millward and J. Titley for allowing us to participate in their sampling program in Cornwall, Carnon Consolidated Tin Mines for access to the Carnon River, and the staff of the Driffold Hotel, Devoran, for their help and cooperation.

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Experimental methods

Water sampling was undertaken in Keithing Burn and its estuary in May 1985 and in the Carnon River and its estuary in June and September 1985. Samples were collected in chromic acid-cleaned glass bottles about 10 cm below the water surface, from either the riverbank or a shallow-bottomed boat, and the pH measured. Samples were stored in the dark at between 1° and 5°C until analyzed.

The mean electrophoretic mobility (U_E) of the suspended particles was measured, without pretreatment, at 25°C in a flat cell with a Rank Mark II microelectrophoresis apparatus adapted for use with a camera and video monitor (Rank Bros., England). This apparatus was interfaced to an Apple IIe microcomputer to facilitate both data processing and the measurement of voltage and velocity for each particle examined (Loder and Liss 1982). U_E measurements were made in the laboratory within 2–12 d of sampling, except for the September survey of the Carnon River. During this survey U_E was measured close to the sampling site within 20 min of sample collection, and experimental parameters were recorded manually.

The experimental techniques used here for the determination of U_E are those developed previously in this laboratory (Hunter and Liss 1982; Loder and Liss 1982, 1985). When Ag-AgCl reversible electrodes were used with the fresh and low-salinity waters from both Keithing Burn and the Carnon River, electrode deterioration occurred. This deterioration was apparent as the formation of a silver chloride precipitate throughout the cell and the reversion of the electrodes to metallic silver. The problem was overcome by using palladium electrodes charged with hydrogen to a H:Pd ratio that avoided problems with residual gassing and Pd dissolution (Neihof and Schuldiner 1960). At salinities $\gtrsim$10‰ the higher currents required for U_E measurement caused gassing or dissolution, so it was necessary to use a cell of reduced cross section (Hunter and Liss 1982). The current again became prohibitive at salinities $\gtrsim$25‰, but Ag-AgCl electrodes could then be used as they did not deteriorate at higher salinities.

The effect of pH on mobility was observed by adding aqueous sodium hydroxide or hydrochloric acid (previously irradiated with UV light to oxidize organic matter) to aliquots of river water and measuring the mobility and pH after 24 h. A further series of experiments was conducted in which particles from a given water sample were resuspended in the supernatant from another sample of different salinity and pH. Particles were separated from their supernatants by centrifuging and then rinsed and resuspended in the new supernatant. Some samples of supernatant were irradiated in silica tubes with UV light from a 1-kW Hanovia UV lamp for 24 h to oxidize organic matter. Oxide-hydroxide precipitates formed during oxidation were removed by centrifugation. All glassware was soaked in chromic acid and rinsed thoroughly in freshly double-distilled water.

Study areas

Fordell-Keithing Burn is an iron-rich stream which drains into the Firth of Forth at Inverkeithing through a small estuary (Loder and Liss 1982, 1985). The stream is highly contaminated by drainage waters which feed into Fordell Burn from an abandoned coal mine (e.g. 0.45-μm-filterable Fe 19.5 ppm, Mn 2.6 ppm, pH 6.6 at the confluence of burn and mine waters: T. Leatherland pers. comm.).

The Carnon River drains a mineralized area in the Falmouth-Truro district of West Cornwall, a region of extensive mining activity in the 19th century. There was little mining in the Carnon Valley in this century up until 1971, from which time the Wheal Jane and Mt. Wellington mines have been intermittently worked for Sn, Cu, and Zn. Figure 1 shows the lower reaches of the Carnon River and its estuary, Restronguet Creek, along with the major inputs and the freshwater and low-salinity sampling sites used in this study. The County adit, Mt. Wellington adit, and Wheal Jane input represent significant mine drainages—acidic and highly contaminated with trace metals, particularly Fe (from pyrite) and Zn. Other

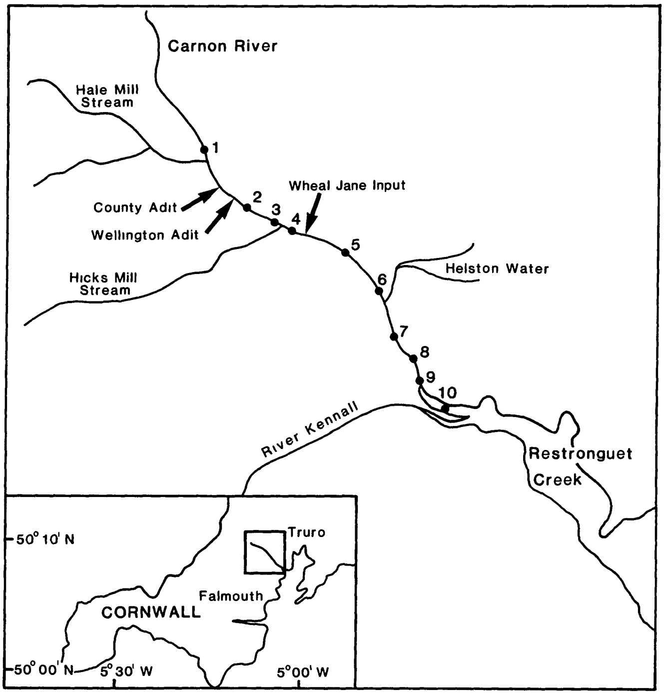

Fig. 1. Map showing the tributaries of the Carnon River and Restronguet Creek (redrawn from Johnson 1984, not to exact scale), and sampling sites 1–10 used in survey 2, September 1985.

tributaries are comparatively less contaminated and lower in flow rate. Restronguet Creek has two major inputs, the Carnon River and the River Kennall, but the Carnon constitutes the major trace element input to the creek. All the tributaries of the Carnon River-Restronguet Creek system are highly variable, both in terms of flow and composition, depending on the rainfall and degree of mining activity. Typical 0.45-μm-filterable ion concentrations (ppm) at site 5 are Na (60–220), K (6–20), Ca (60–200), Mg (8–15), Cl (270–870), SO_4^{2-} (60–300), F (2–4), Al (1.2–3.5), P (0.01–0.14 as PO_4^{3-}), Fe (3–12), Zn (4–14), Mn (1–2), Cu (0.5–1.0), and total organic carbon (2.1) and pH 3.4–5.0 (Johnson 1984, 1986). Our analyses of 0.45-μm-filterable Na, K, Ca, Mg, Cl^-, SO_4^{2-}, and Fe and pH in samples collected in this study are comparable. Speciation studies of the trace metals indicate predominantly labile inorganic species (Johnson 1984). Together the tributaries combine to cause considerable trace-element contamination of the waters and sediments of the river and estuary (Hosking and Obial 1966; Thornton et al. 1975; Boyden et al. 1979; Thorne 1983; Johnson 1984, 1986).

Results and discussion

Fordell-Keithing Burn—The U_E values of suspended particles in Fordell-Keithing Burn and its estuary are shown in Fig. 2a. The shaded area shows the U_E range found in natural waters in other studies (Hunter and Liss 1979, 1982; Loder and Liss 1982; Tipping et al. 1981; Hunter 1983). Open symbols represent a previous survey in which U_E values for samples of salinity $<8‰$ were found to fall outside the U_E range found typically. This anomaly was attributed to incomplete organic coatings on inherently positively charged iron oxide-hydroxide particles (Loder and Liss 1982, 1985). Closed circles show U_E values of suspended particles in the river and estuary measured in the present study. A U_E typical of natural waters is observed both upstream of the mine-water input and at salinities $\gtrsim 5‰$. The U_E immediately downstream of the mine-water input is small but still negative (−0.3

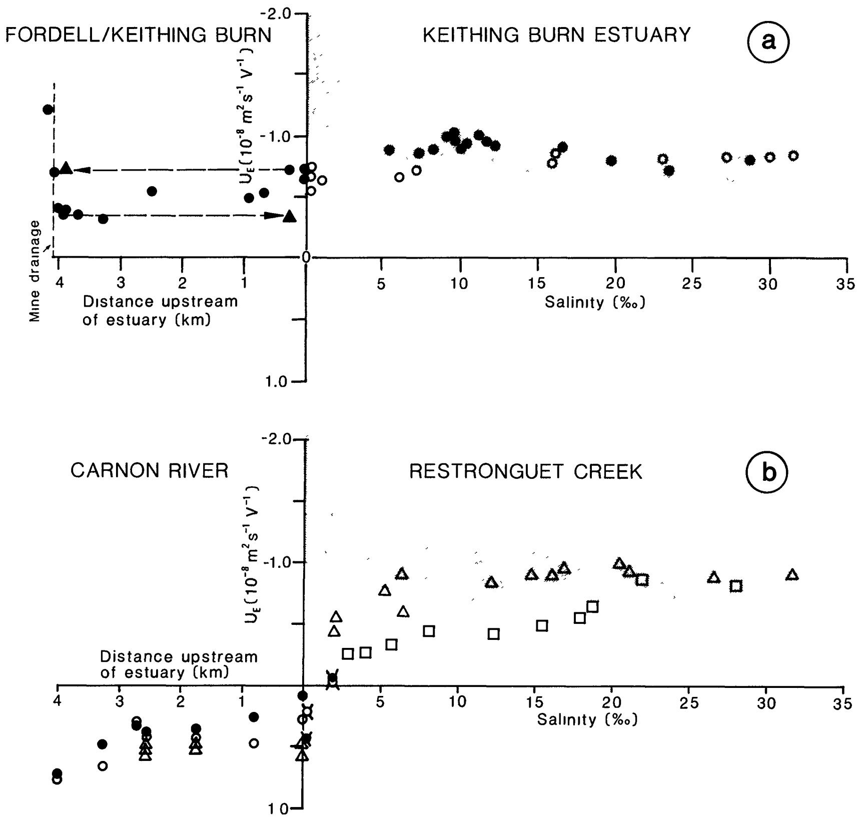

Fig. 2. Mean electrophoretic mobilities (U_E) of suspended particles as a function of distance upstream from the estuary and salinity. Shaded area represents the spread of U_E values in other natural waters. a. Fordell-Keithing Burn and its estuary: ○–Loder and Liss 1985; ●—this study; arrows—U_E change when particles (●) are resuspended in river water from ▲ (*see text*). b. Carnon River and its estuary (Restronguet Creek): survey 1 (June 1985) △—floodtide and □—ebbtide, 2–12 d of storage; survey 2 (September 1985) ●, ⧗—river (turbidity maximum) samples analyzed within 20 min of collection, ○, ⧖—same samples after 6 d of storage.

to -0.4×10^{-8} m^2 s^{-1} V^{-1}), becoming increasingly negative farther downstream.

The burn has a pH of 6.3 at 4 km, increasing downstream to 7.9 at 300 m. The pH of these samples remained constant (±0.2) during sampling, storage, and centrifugation and resuspension procedures. When particles from 4 km upstream of the estuary were resuspended in supernatant from 300 m upstream of the estuary, no change in U_E was observed (right-facing dashed arrow in Fig. 2a). Similarly, when particles from 300 m were resuspended in supernatant from 4 km, the U_E again remained unchanged (left-facing dashed arrow in Fig. 2a). The increase in negative U_E observed between 4 km and 300 m is therefore not due to the influence of differences in inorganic water composition, including pH, but apparently represents different particle surfaces, at least at the electrokinetic plane of shear. The anomalously low U_E of particles in the burn therefore suggests the at least partial absence of the organic coatings which are apparent on the surfaces of suspended particulates in most natural waters. The increase in negative U_E downstream of the mine-water input could therefore either reflect progressively more complete organic coatings or different inorganic particle surfaces.

All U_E measurements for Fordell-Keithing Burn and its estuary, including those of Loder and Liss (1982, 1985), were made within 2–12 d of sample collection. This storage period has been demonstrated to not significantly change U_E in typical natural waters (Hunter and Liss 1982). In these Fe-Mn-rich waters, however, natural oxidation causes the formation of new oxide-hydroxide over such a time scale, possibly modifying particle surfaces. The assumption that the U_E data presented represent the U_E of particles in the burn may therefore be incorrect; the anomalously low negative U_E values observed in the burn and estuary could be artifacts of sample storage.

Carnon River-Restronguet Creek—The U_E values of suspended particles in the Carnon River and its estuary, Restronguet Creek, are shown in Fig. 2b. Open symbols represent samples stored for 2–12 d before U_E measurement, and closed symbols represent measurements made within 20 min of sample collection. The results of survey 1 indicate that suspended particles from the river and mixing zone have a positive U_E and that those in the estuary have a negative U_E. Data from survey 2 show that suspended river particles display a positive U_E 20 min after sample collection and that storage for several days either causes some increase in positive U_E or no significant change. X-ray diffraction and electron microscopy studies (Johnson 1984, 1986) indicate that most particles are a composite of silica-rich crystalline clays and loosely structured amorphous iron hydroxides, and the shape and hysteresis of a nitrogen adsorption-desorption isotherm indicates a ferric precipitate derived from the oxidation and hydrolysis of ferrous iron (Marsh et al. 1984). These results indicate surfaces dominated by iron oxide-hydroxide phases. In the absence of organic coatings, it would be expected that iron oxide-type surfaces would exhibit positive U_E values over the pH range of the river, 3.5–5.0 (Parks and de Bruyn 1962; Tipping 1981). The positive U_E of suspended particles 20 min after sampling remained constant over a period of at least several hours, strongly suggesting that these data represent the in situ U_E of the particles.

In view of the negative U_E conferred on particles by natural organic coatings, these results represent the first experimental evidence of suspended particles with U_E controlled by an inorganic surface. This surface is defined by the electrokinetic plane of shear, and its charge characteristics are controlled by the solid particle surface and ionic species and complexes adsorbed within this plane of shear. All suspended particles in the estuary downstream of the turbidity maximum (>2‰) have negative mobilities (Fig. 2b). Possible contributory factors are aging, the adsorption of organic or inorganic matter onto Carnon River particles, the change in pH and ionic composition through the estuary, and particulate inputs from the River Kennall, bottom sediments, and the sea.

Table 1. U_E data ($10^{-8}\ \mathrm{m^2\ s^{-1}\ V^{-1}}$), pH, and conductivity ($10^{-1}\ \Omega^{-1}\ \mathrm{m^{-1}}$) of samples from sites 1–10 analyzed within 20 min of collection, survey 2, and standard deviation (SD) data from both surveys.

Site	U_E	SD	Cond.	pH
1	–	–	0.27	5.9
2	+0.67	0.13	1.80	3.6
3	+0.48	0.10	1.81	3.5
4	+0.33	0.08	1.07	3.6
5	+0.38	0.07	2.66	3.8
6	+0.35	0.09	2.65	4.2
7	+0.26	0.05	2.55	4.3
8	+0.06	0.16	2.68	4.9
9 TM*	+0.43	0.37	2.29	5.5
10 TM	−0.07	0.31	5.32	5.9
Estuary downstream of TM		0.09–0.19		

* Turbidity maximum.

Suspended particles in the Carnon River—U_E data, pH values, and conductivities for samples analyzed within 20 min during survey 2 are given in Table 1. All particles observed at site 2 originate from the Mt. Wellington and County adits–Hale Mill stream, as water from site 1 showed virtually no visible particles in the electrophoresis cell. Inspection of conductivity perturbations identifies the major dissolved inputs to the river during the survey as the Mt. Wellington and County adits–Hale Mill stream, Hicks Mill stream, and the Wheal Jane input. The particle load at site 5 was visually much greater than that at site 4, indicating that the Wheal Jane particulate input was the source of most Carnon River particles entering the estuary. Samples from sites 5, 6, 7, and 8 can therefore be visualized as Wheal Jane suspended particulate material progressing downstream toward the

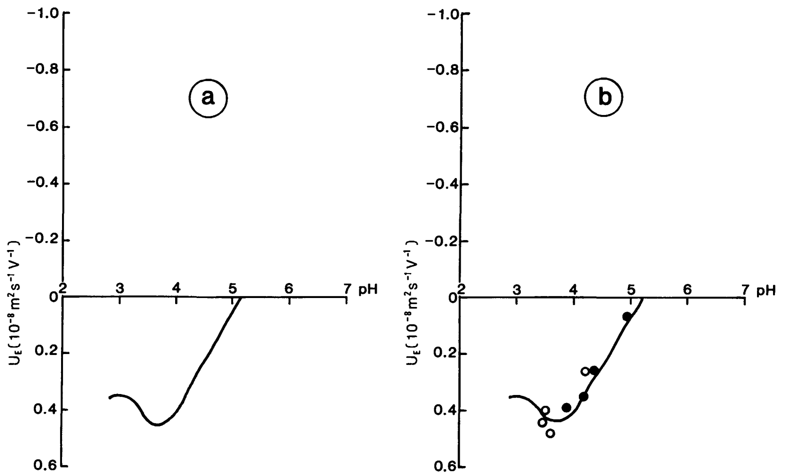

Fig. 3. a. U_E of suspended particles from site 5 as a function of pH of the total sample 24 h after NaOH or HCl addition. b. U_E of suspended particles from sites 5, 6, 7, and 8 as a function of pH; 20 min (●) and 6 d (○) after sample collection. The curve from panel a is superimposed.

estuary, during which passage U_E decreases to almost zero and pH increases.

All river samples collected during survey 2 were reanalyzed after 6 d, as shown in Fig. 2b. Storage caused a decrease of up to 0.8 pH units, an increase in conductivity, and a significantly more positive U_E for half the samples examined, but with no significant change for the rest. Filtered (0.45 μm) river water precipitated an oxide-hydroxide phase within 2 d, which strongly suggests the formation of additional oxide-hydroxide surfaces during sample storage. The decrease of pH is typical of the oxidation-hydrolysis of iron to form oxide-hydroxide precipitates. The increase in conductivity probably largely reflects this pH decrease, owing to the significantly higher molar conductivity of the H_3O^+ ion relative to other hydrated ionic species.

The curve in Fig. 3a represents U_E values measured 24 h after adding NaOH or HCl to aliquots of untreated river sample from site 5. Figure 3b shows the U_E data for the fresh and stored samples from sites 5, 6, 7, and 8 (i.e. particulates derived from Wheal Jane) with the curve from Fig. 3a superimposed. These data correlate well with the pH curve, suggesting first that the U_E decrease observed for fresh samples from sites 5–8 reflects the effects of pH changes in the river and, second, that the U_E increase caused in some samples by storage is at least partly attributable to the concomitant pH decrease. This correlation of both the stored and the fresh samples with the curve also suggests that any new oxide-hydroxide surfaces precipitated during storage for 6 d have similar surface charge characteristics to the river particle surfaces. This supports the conclusion that the positive U_E values observed in the river reflect U_E control by an inorganic surface.

Suspended particles in Restronguet Creek—A strong turbidity maximum was observed at the confluence of river and seawaters. Previous work suggests that >95% of <0.45-μm iron in the Carnon River is in the <500 mol wt fraction and is not associated with organic material (Mill 1980; Johnson 1984, 1986), i.e. not present as the particulate iron-organic matter colloids widely observed in rivers. Further, 40–50% of <0.45-μm iron is typically removed in the turbidity maximum zone in Restronguet Creek (Johnson 1984). Along with the sudden increase in pH on mixing with seawater, this suggests that a major factor in iron removal in the mixing zone is precipitation of new oxide-hydroxide material rather than aggregation of particulate iron-organic matter colloids as observed in more typical river–estuary systems (Boyle et al. 1977; Sholkovitz et al. 1978; Bale and Morris 1981;

Mayer 1982). It therefore seems that particles at the turbidity maximum are composed largely of riverine material (possibly aggregated), new oxide-hydroxide phases formed in situ, and resuspended bottom sediment.

Samples from sites 9 and 10 represent the turbidity maximum at <1‰ and its leading edge at 2‰. These samples show a wide range of individual particle mobilities, both positive and negative (-0.7 to $+1.4 \times 10^{-8}$ m^2 s^{-1} V^{-1}), reflected by their markedly larger standard deviations compared to river and other estuary samples (Table 1). Storage for 6 d reduces the standard deviations to values typical of estuarine samples, and, in contrast to the river samples discussed in the last section, storage of the <1‰ sample causes a decrease in positive U_E (Fig. 2b) despite a decrease in pH. This U_E behavior and the high standard deviations observed probably reflect the sudden physical and chemical perturbation caused by seawater mixing, i.e. particle surfaces controlled by precipitation, aggregation, resuspension, adsorption-desorption, and inorganic and organic complexation processes at varying degrees of equilibrium.

Restronguet Creek is a shallow estuary, and resuspension of bottom sediments by tidal action was observed. At the river end of the creek, the surface sediments are ochreous, graduating to gray-brown at the seaward end of the estuary. Ebbtide samples of <20‰ salinity all contained high loads of resuspended ochre sediment from the river end of the estuary. Some floodtide samples between 6 and 18‰ contained gray-brown resuspended sediment from the middle of the estuary. If U_E control is not exerted by organic coatings in these samples, then different mobility characteristics would be expected for particles from the two tides at salinities <20‰. These differences are clearly illustrated by the contrasting ebb and floodtide U_E profiles shown in Fig. 2b.

We have presented evidence for river particle mobility being governed by oxide-hydroxide surfaces. Surface coastal waters contain sufficient surface-active organic material to control the U_E of their suspended particle populations (Neihof and Loeb 1972, 1974; Loeb and Neihof 1975, 1977; Hunter 1980). Thus, at high salinities one would expect predominantly marine particles with natural organic coatings, exhibiting a U_E typical of coastal surface waters. Such U_E values are observed, implying that the end members of the estuary represent particles with zero and complete coverage by organic coatings as measured by electrophoresis. The relationship between U_E and extent of organic coverage of natural particles is not known, but several workers have demonstrated a gradation from positive to negative U_E as a function of organic adsorption in simplified systems (Neihof and Loeb 1974; Hunter 1980; Tipping 1981; Tipping and Cooke 1982). The gradation of negative mobilities observed through Restronguet Creek may therefore reflect gradually increasing organic coverage exerting U_E control. However, U_E control by physical-chemical inorganic processes operating on inorganic surfaces (e.g. water column chemistry, sedimentary diagenesis before particle resuspension) may also be important.

Figure 4 shows U_E against pH for all estuarine data with Fig. 3b superimposed. Additionally, Fig. 4 shows the effects of suspending floodtide estuarine particles from water of various salinities in river water (pH 3.3) from site 5 (dashed arrows). Suspended particles from 2.5‰ salinity show charge reversal to a U_E typical of a river sample. Particles from waters of salinity 6.3, 12.0, and 16.8‰ become less negative and 31.5‰ become more negative. The expected effect of the change in ionic strength on immersion in river water would be a more negative U_E; this effect is observed only at 31.5‰. That is, estuarine particles immersed in river water assume a wide range of positive and negative U_E values. This result reveals the variety of particle surfaces in the estuary, which in turn reflects different particulate inputs and the effect of the estuary on these surfaces. If natural organic coatings were in evidence at all salinities, this variety would not be expected. The behavior of the 2.5‰ sample indicates surfaces similar to the river particles, whereas at 6.3‰ and above the surfaces are different.

Figure 4 shows that a linear extrapolation of the pH curve intersects this 2.5‰ sample,

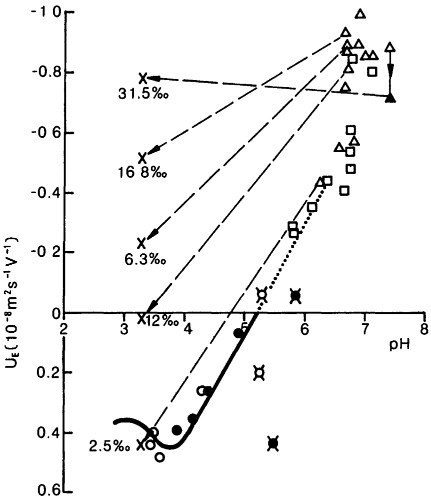

Fig. 4. U_E of suspended particles from Restronguet Creek as a function of pH, with Fig. 3b superimposed: △—floodtide and □—ebbtide, 2–12 d of storage. Dashed arrows indicate U_E change when particles from △‰ are suspended in river water from site 5, pH 3.3. (△—▸—▲ represents decrease in U_E of particles from 31.5‰ during several weeks of storage before resuspension in river water; no such decrease occurred with other samples.) Turbidity maximum samples after 20 min (✖) and 6 d (⊠) of storage. Dotted line—linear extrapolation of pH curve to floodtide sample at 2.5‰ salinity.

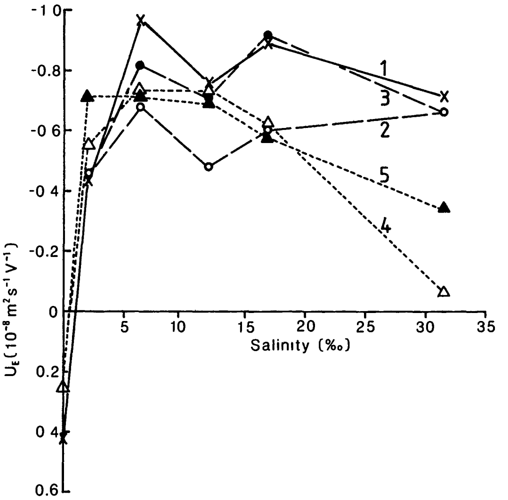

Fig. 5. U_E of river particles suspended in estuarine water of various salinities at a constant particle : water ratio. Curve 1—untreated estuarine samples; curve 2—river particles in untreated estuarine water, one soak; curve 3—curve 2, repeated soaks; curve 4—river particles in organic-free estuarine water, one soak; curve 5—curve 4, repeated soaks.

as well as the three ebbtide samples from <8‰, strongly suggesting river-type surfaces. The rest of the samples (excepting those from the turbidity maximum) appear to form two groups. The group clustered at the end of the extrapolated curve represents all suspended particles <2.5‰ salinity and resuspended samples collected toward the river end of the creek. The proximity of this group to the curve may be indicative of river-type surfaces. This river-type character is not an artifact of storage; 2–12 d of sample storage does not seem to affect the U_E of particles collected from downstream of the turbidity maximum. This probably reflects exhaustive precipitation of new oxide-hydroxide having already occurred. The second group clusters away from the curve, suggesting nonriver-type surfaces and represents suspended and resuspended particles from higher salinities. This assessment of river-type particle surfaces is consistent with the results of resuspending the estuarine particles in river water (Fig. 4).

The results given in Fig. 4 also show that fresh U_E data from the turbidity maximum do not correlate well with the pH curve. They must reflect nonriver-type surfaces. However, correlation with the pH curve indicates river-type surfaces for the stored turbidity maximum sample at 2‰ salinity and for other samples just downstream of the turbidity maximum. A possible explanation is that this turbidity maximum anomaly reflects the sudden physical and chemical perturbation caused by seawater mixing and that time, either as storage or downstream flow, allows a new equilibrium to be approached at the particle surface.

The effects of suspending river particles in estuarine waters at five salinities are shown in Fig. 5. Curve 1 represents the natural untreated samples, curve 2 represents river particles immersed in estuarine water at a similar particle : water ratio, and curve 3 represents curve 2 after repeated soakings of the same particles in more water. Comparison of curves 1 and 3 indicates that the natural U_E profile through the estuary is not inconsistent with riverine particles comprising the major particulate input. River particles immersed in the 2‰ salinity water attain the U_E of 2‰ particles after one soak, giving further evidence that 2‰ particles have river-type surfaces. At higher salinities increases in negative U_E after repeated soaks are observed. They may be indicative of the progressive adsorption of organic matter (Neihof and Loeb 1974; Hunter 1980).

In an attempt to resolve this question, these experiments were repeated after first irradiating the estuary waters with UV light to destroy organic matter. Curve 4 shows the results of one soak; repeated soaks gave curve 5. These curves show that positively charged river particles assume a negative U_E in estuarine waters even after the removal of organic matter, presumably owing to changes in water composition altering the species and complexes adsorbed within the electrokinetic plane of shear. Only at 31.5‰ does U_E differ significantly from the particles immersed in untreated water. Repeated soaks in irradiated waters do not increase negative U_E for samples at salinities of 6.3, 12.0, and 16.8‰, whereas they do in the untreated waters. This finding indicates that the adsorption processes evident in untreated waters are not occurring with these irradiated waters. Additionally, settled sediment in the irradiated waters >2‰ was much easier to disperse by shaking than the corresponding sediment in untreated waters, implying different particle–particle interactions, and hence different particle surfaces. As UV irradiation oxidizes organic material, these observations implicate the adsorption of organic matter by river particles immersed in estuarine water from 6.3‰ and above. One might then speculate that the floodtide estuarine particles from salinities >6.3‰ will also have adsorbed organic matter. A comparison of curves 1, 3, and 5 then suggests that the formation of any such organic coatings significantly affects U_E at 16.8‰ and above.

However, repeated soaks in irradiated waters at 2 and 31.5‰ do cause an increase in negative U_E. As well as oxidizing organic matter, irradiation precipitates ochreous oxide-hydroxide from all except the 31.5‰ sample. The oxidation may also alter the speciation of other dissolved constituents. Thus, irradiation changes the ionic composition of the waters, although no pH change is observed. This composition change may affect the U_E, particularly if the ions implicated participate in adsorption processes within the electrokinetic plane of shear. Some evidence for such an effect is shown in curve 4 at 0‰; the river particles, reimmersed in their own irradiated supernatant, decrease in U_E from +0.42 to +0.25 $\times 10^{-8}$ m^2 s^{-1} V^{-1}. This change makes a more rigorous interpretation of curves 4 and 5 difficult.

We conclude that the Carnon River-Restronguet Creek river–estuary is atypical of natural waters, since it contains suspended particles with and without organic coatings, and hence a range of positive, zero, and negative mobilities. By contrast, the suspended particles of a typical natural water are coated with organic matter and bear solely negative mobilities. Thus, particle surfaces are physically and chemically unusual in the river–estuary studied here, which suggests that particle–particle and particle–water interactions might be governed by different processes than those observed under more normal conditions. The Carnon River and Restronguet Creek therefore potentially constitute a "natural laboratory" for investigating the relative roles of organic and oxide-hydroxide surfaces, and their differing surface charge characteristics, in the behavior of suspended particles in natural waters.

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