summarizes the results of these calculations as a function of *p*H. The shape of this curve and the location of the inflection point suggest that the *p*H dependence is caused by a difference in the reaction rate of HSO_3^- and SO_3^{2-} since the *pK* of this equilibrium is 7.20 (*6*).

The measured rate constants (in liters per mole per minute × 10^{-4}) for several representative organic chloramines at *p*H 7 and 25°C are as follows: methylamine, 26; N-α-acetylysine, 13; alanine, 7; leucine, 14; and *N*-chloroalanylalanylalanine, 0.5. The rate constants for the other amines are greater by at least an order of magnitude than that for the *N*-terminal amino group of the peptide.

We also conducted several experiments in which *N*,*N*-dichloroalanylalanylalanine was prepared by the addition of NaOCl at a molar ratio of NaOCl to peptide of more than 7:1. After addition of excess SO_3^{2-}, the rate of reappearance of the peptide was the same as that seen in the case of the monochloropeptide. We interpret this as a stepwise reaction in which one chlorine is reduced very rapidly and the remaining monochloropeptide reacts as usual.

The reaction of organic bromamines with aqueous SO_3^{2-} is also of interest because they are formed during the chlorination of estuarine and marine waters (*7*). We have found that, in contrast to the case for the organic chloramines, *N*-bromoalanylalanylalanine reacts completely with SO_3^{2-} within 15 seconds.

Earlier attempts to detect these stable residuals with the standard analytical techniques such as the amperometric and *N*,*N*-diethyl-*p*-phenylenediamine methods (*8*) were unsuccessful when excess SO_3^{2-} was present. This observation appears to be due to the fact that these methods measure chloramines by first reacting iodide with the chloramine to form iodine. The iodine is then the species that is determined. However, in the present case the iodine reacts with the excess SO_3^{2-} to form iodide and sulfate. The apparent result then is that no chloramine is present.

The consequence of this interference with the standard analytical methods and the surprising stability of some organic chloramines to reduction by SO_3^{2-} is that an unknown concentration of oxidizing residual is present in chlorinated effluents even after chemical dechlorination. Under some circumstances these residuals could be quite long-lived. For example, the half-time of the reaction between a solution of $10^{-6}M$ *N*-chloroalanylalanylalanine and $10^{-6}M$ SO_3^{2-} at *p*H 7 and 25°C is approximately 3 hours. Whether this finding is of any environmental significance remains to be seen as the impact is dependent on the actual amounts of these types of compounds formed during chlorination and their potential toxicities to aquatic organisms.

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References and Notes

1. L. W. Hall, G. R. Helz, D. T. Burton, *Power Plant Chlorination: A Biological and Chemical Assessment* (Ann Arbor Science, Ann Arbor, Mich., 1981).
2. G. G. White, *Handbook of Chlorination* (Van Nostrand Reinhold, New York, 1972), p. 346.
3. C. R. Lytle and E. M. Perdue, *Environ. Sci. Technol.* **15**, 224 (1981).
4. J. C. Morris, in *Principles and Applications of Water Chemistry*, S. D. Faust and J. V. Hunter, Eds. (Wiley, New York, 1967), p. 23.
5. L. E. Conroy, W. J. Maier, Y.-T. Shih, paper presented at the 179th national meeting of the American Chemical Society, Division of Environmental Chemistry, Houston, Texas, 23–26 March 1980.
6. W. D. Scott and P. V. Hobbs, *J. Atmos. Sci.* **24**, 54 (1967).
7. G. R. Helz, R. Sugam, R. Y. Hsu, in *Water Chlorination, Environmental Impact and Health Effects*, R. L. Jolley, H. Gorcher, D. H. Hamilton, Eds. (Ann Arbor Science, Ann Arbor, Mich., 1978), vol. 2, p. 209.
8. *Standard Methods for the Analysis of Water and Wastewater* (American Public Health Association, Washington, D.C., ed. 14, 1976), pp. 322–325 and 329–334.
9. Supported by the State of Maryland Power Plant Siting Program.

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Role of Natural Colloids in the Transport of Hydrophobic Pollutants

Abstract. *The sorptive properties of natural estuarine colloids were investigated, with the herbicides atrazine and linuron used as model pollutants. Linear Freundlich adsorption constants for atrazine and linuron were 1850 and 6750, respectively. These high values indicate that natural colloids have the potential to be important substrates in the transport of hydrophobic contaminants in aquatic environments.*

The fate of organic pollutants in natural waters depends in part on the sorptive behavior on sediments and suspended particulates. In addition to affecting the mobility of the pollutants, sorption may directly contribute to the degradation of chemicals by surface-associated chemical and microbial processes (*1*). Hence, sorption equilibria are important parameters in assessing the environmental fate and toxicological impact of organic pollutants in aquatic systems. Although the role of natural colloids in the transport and toxicity of metals has long been recognized (*2*), the corresponding quantitative studies on trace organic species are absent from the literature. Thus, a key link in our understanding of the transport, persistence, and toxicology of organic pollutants is missing. We present here what we believe are the first quantitative data for the sorption equilibria of the widely used herbicides atrazine and linuron on estuarine colloidal material. In addition, physical parameters, such as *p*H and salinity, that control sorptive behavior on these substrates are discussed.

Natural water samples (20 liters) of various salinities (1 to 19 per mil) were collected at 0.5 m below the surface in Chesapeake Bay from stations on the Choptank and Patuxent rivers in Maryland. We filtered the samples through prewashed 0.45-μm Millipore filters to remove suspended particulate material and concentrated them by ultrafiltration, using an Amicon model H_1P_5 hollow fiber system having a nominal molecular weight cutoff of 5000. Sample volumes were reduced approximately 50-fold, and the result was an enriched colloidal fraction. This fraction was divided into several 50- to 70-ml portions, and 1 liter of ultrafiltrate containing a known amount of atrazine or linuron was added to each. The spiked samples were equilibrated in a shaker for 18 hours at 20°C and then recirculated through the hollow fiber system to separate the colloidal and ultrafiltrate (dissolved) fractions. The hollow fibers were rinsed with about 20 ml of distilled water to ensure complete removal of the enriched colloidal matter. We determined the herbicide contained in each fraction by high-performance liquid chromatography on a μBondapak-phenyl column (300 mm by 2.1 mm inside diameter), using an isocratic mixture (constant mixture of two solvents with different solubility parameters) of acetonitrile and water (35:65) at a flow rate of 1.5 ml/min. The column effluent was passed through an ultraviolet detector set at a wavelength of 254 nm.

The organic carbon content of the enriched colloidal fraction was measured on an Oceanography International analyzer (Table 1). Results on blanks indicated that less than 2 percent of the carbon in the samples was due to material from the Millipore filters. Estuarine colloidal matter has been characterized (*3*) as a proteinaceous-carbohydrate polymer that is associated with varying amounts of poorly crystallized clay minerals and trace metals (*4*).

Figure 1 shows that the 20°C equilibrium adsorption isotherms of atrazine and linuron onto estuarine colloidal matter from natural water ultrafiltrates were linear over the ranges of solution concentrations tested. These ranges were selected such that neither the sorptive capacity of the colloids nor the water solubility of the compound would be a limiting factor. Because no deviations from linearity were observed, the results suggest that the amount of herbicide adsorbed in these experiments was within the sorptive capacity of the colloids.

The amount of sorbed herbicide is normalized and reported on the basis of the amount per gram of carbon because (i) the amount of carbon associated with the colloid was the most precise measure available for monitoring the amount of colloid present in both the bulk water and the colloid-enriched water and (ii) organic matter is the portion of a variety of environmental substrates (sediments, soils, microorganisms) that controls the adsorptive behavior of a wide variety of nonpolar organic compounds (*5–8*).

The slopes of the isotherms determined by linear regression (Table 1) correspond to the sorption constants (K_{oc}), which are derived from the linear form (n = 1) of the Freundlich equation

$$C_s = K_d \, C_w^{1/n}$$

where C_s is the concentration of substrate sorbed, C_w is the concentration of substrate in solution, and K_d and n are constants. This equation has been used widely for the empirical description of the sorption of a substrate in soil-water or sediment-water systems. In several soil and sediment systems, the correlation of organic matter to the K_d of neutral (nonpolar) molecules is 0.9 or more (*6–8*). Therefore, the K_d values are normalized to the organic carbon content of the sorbent. These K_{oc} values correlate with both the octanol-water partition coefficient and the water solubility of the compound being sorbed (*6, 8, 9*). Values of K_{oc} for atrazine and linuron sorbed on soils range from 47 to 394 and from 124 to 2678, respectively; the mean values are 170 and 670, respectively (*10*).

Table 1. Sorption constants for atrazine and linuron on estuarine colloids.

Sample code*	Date	Salinity	Total organic carbon (mg/liter) of the enriched colloidal fraction	K_{oc}†
CL_1AT	August 1980	1.24	98.6	13,600
CM_1AT	August 1980	9.92	108.5	4,860
CH_1AT	August 1980	14.2	104.6	6,990
CL_2AT	September 1980	1.50	65.5	8,540
CM_2AT	September 1980	5.71	74.2	7,930
CH_2AT	September 1980	17.0	59.3	4,840
P_rH_1AT	February 1981	19.1	33.5	1,690
P_rH_3AT	May 1981	14.6	44.0	1,850
P_rH_4LIN	May 1981	13.5	49.0	6,760
P_rH_5LIN	May 1981	14.5	52.5	6,210

*C = Choptank River samples; P_r = Patuxent River samples; L, M, H = low, medium, or high salinities, respectively; AT = atrazine; LIN = linuron. †Correlation coefficient (r^2) = >.992.

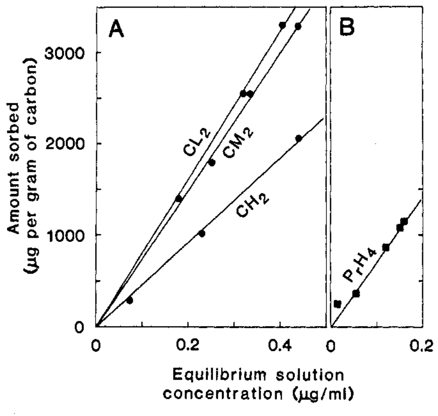

Fig. 1. Equilibrium adsorption isotherms at 20°C of (A) atrazine and (B) linuron on estuarine colloidal matter. The sample code is explained in Table 1.

The effects of salinity and pH on the sorption of atrazine and linuron are shown in Fig. 2. Significant changes were observed in the K_{oc} values for atrazine when the salinity was decreased by a factor of 2. This observation is consistent with the general pattern of results shown in Fig. 1 but is opposite to the trend that would be predicted as a result of the "salting out" of the hydrophobic herbicide; this finding suggests that changes in the colloid itself are responsible for the shift in K_{oc}. A significant decrease in sorption was observed when the ambient pH of 7.98 was increased to 9.0 or decreased to 5.0.

The high K_{oc} values for colloidal matter suggest that atrazine and linuron are strongly bound. On an organic carbon basis, the colloidal material is on the order of 10 to 35 times better as a sorptive substrate for the herbicides than sediment or soil organic matter. However, the relative strengths of sorption of the two compounds on colloidal matter as reflected in the ratio of the K_{oc} value of atrazine to linuron appear to be the same as the ratio of these K_{oc} values on soil-sediment (170 versus 670 for soil as opposed to 1850 versus 6750 for colloids). Wu *et al.* (*11*) observed that atrazine concentrated in the surface microlayers of estuarine waters at concentrations of 150 to 8850 μg/liter. This represented typically an enrichment of 10 to 30 over bulk water atrazine concentrations. If we assume that this enrichment is due to sorption by the hydrophobic organic matter that is present at the air-water interface and assume also that an average colloidal organic carbon content of this material is 5 mg/liter, then the resultant K_{oc} values would be on the order of 2000. This value compares to our K_{oc} values within a factor of 1 to 5.

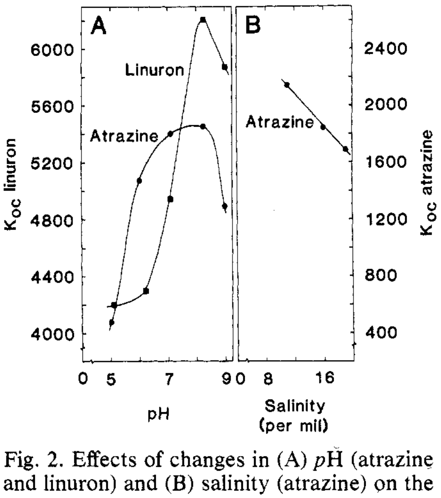

Fig. 2. Effects of changes in (A) pH (atrazine and linuron) and (B) salinity (atrazine) on the K_{oc} values.

Two hypotheses that may explain the difference between K_{oc} values observed on soil-sediment and on colloidal matter are suggested. First, although K_{oc} values are reported on the basis of total organic carbon for a soil or sediment, all the organic carbon is not available as a sorptive surface. Soil-sediment organic matter is itself sorbed to a highly porous and irregular inorganic matrix, often occupying or filling in micropores in the structure. If it can be assumed that the soil-sediment organic matter is not a monomolecular film, the K_{oc} values calculated on a total-carbon basis may be low by one to two orders of magnitude. This would shift the average K_{oc} for atrazine to values in a range comparable to that observed in these experiments. Alternatively, the surface acidity of sediment or soil clay particles may have the effect observed here of decreasing the sorptive capacity of the organic matter.

These results suggest that natural colloids may be important in the transport of hydrophobic contaminants in the aquatic environment. Furthermore, the partitioning of solutes onto these colloids is highly dependent on bulk water characteristics, such as *p*H and salinity. The extreme *p*H dependence of these biopolymers also suggests that the sorptive properties of colloids must be studied under ambient conditions if meaningful data are to be obtained.

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References and Notes

1. S. U. Khan and M. Schnitzer, *J. Environ. Sci. Health Part B* **13**, 229 (1978); H. D. Skipper and V. V. Volk, *Weed Sci.* **20**, 344 (1972); D. D. Kaufman and J. Blake, *Soil Biol. Biochem.* **2**, 73 (1970).
2. A. Siegel, in *Organic Compounds in Aquatic Environment*, S.D. Faust and J. V. Hunter, Eds. (Dekker, New York, 1971), p. 265; J. B. Andelman, in *Trace Metals and Metal-Organic Interactions in Natural Waters*, P. C. Singer, Ed. (Ann Arbor Science, Ann Arbor, Mich., 1974), p. 57; M. R. Hoffman, E. C. Yost, S. J. Eisenreich, W. J. Maier, *Environ. Sci. Technol.* **15**, 655 (1981).
3. A. C. Sigleo, G. R. Helz, W. H. Zoller, *Environ. Sci. Tech.* **14**, 673 (1980); A. C. Sigleo, T. C. Hoering, P. E. Hare, *Carnegie Inst. Washington Yearb.* **79**, 394 (1980).
4. A. C. Sigleo and G. R. Helz, *Geochim. Cosmochim. Acta* **45**, 2501 (1981).
5. G. W. Bailey and J. L. White, *J. Agric. Food Chem.* **12**, 324 (1964).
6. S. W. Karickhoff, D. S. Brown, T. A. Scott, *Water Res.* **13**, 241 (1979).
7. J. C. Means, J. J. Hassett, S. G. Wood, W. L. Banwart, in *Polynuclear Aromatic Hydrocarbons*, P. W. Jones and P. Leber, Eds. (Ann Arbor Science, Ann Arbor, Mich., 1979), pp. 327–340.
8. J. C. Means, S. G. Wood, J. J. Hassett, W. L. Banwart, *Environ. Sci. Technol.* **14**, 1524 (1980).
9. C. T. Chiou, L. J. Peters, V. H. Freed, *Science* **206**, 831 (1979).
10. P. S. C. Rao, J. M. Davidson, V. E. Berkheiser, L. T. Ou, J. J. Street, W. B. Wheeler, T. L. Yuan, *Retention and Transformation of Selected Pesticides and Phosphorus in Soil-Water Systems: A Critical Review* (Environmental Protection Agency, Washington, D.C., in press).
11. T. L. Wu, *J. Environ. Qual.* **9**, 459 (1980).
12. These experiments were supported by Environmental Protection Agency grant R805932. We thank J. J. Cooney and G. R. Helz for their helpful comments on this manuscript. Contribution No. 1231 of the Center for Environmental and Estuarine Studies of the University of Maryland. Work reported here is part of a dissertation to be submitted by R.W. to the graduate school of the University of Maryland for the degree of Ph.D.

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The High-Velocity Core of the Western Boundary Undercurrent at the Base of the U.S. Continental Rise

Abstract. *The Western Boundary Undercurrent is a high-velocity, contour-following bottom current that flows southwesterly on the U.S. Atlantic continental margin. A high-velocity core of the Western Boundary Undercurrent is delineated by an analysis of underlying sediments, which are characterized by coarse particle sizes and efficiently aligned magnetic grains in a zone from 4440 meters at the base of the rise to 5200 meters on the adjacent abyssal plain.*

The Western Boundary Undercurrent (WBUC) is a high-velocity bottom current that flows southwesterly on the continental margin of the eastern United States. This westward-intensified bottom current consists of North Atlantic deep water that is formed in the Norwegian Sea, and it flows as a contour-following current along the continental slope and rise (*1–3*). The WBUC location has traditionally been inferred from current meters and bottom photographs of sea-floor morphology (*4*) on the continental slope and rise. The exact WBUC location and velocity, however, are not well understood. Early studies placed the WBUC at a depth of less than 3000 m (*2*); later studies placed it deeper than 3000 m (*3, 4*), but in none of these studies was the eastern margin of the WBUC identified.

During the last decade studies have suggested that the current is present at a depth from approximately 1500 m to more than 5000 m (*5*). Although the WBUC appears to flow throughout the depth range, the high-velocity core of the WBUC is more restricted. A problem arises, however, because there is no consensus on the definition of the high-velocity WBUC along the continental slope and rise. Fine sediment is transported as a nepheloid layer (*5, 6*), which is intensified along the lower continental rise (*6*). Palynomorphs on the slope and rise are displaced far to the south of probable source areas (*7*) as a result of the southwesterly transport to the WBUC. Recent evidence for the WBUC, however, was found near the base of the Nova Scotian continental rise by investigators of the High-Energy Benthic Boundary Layer Experiment (HEBBLE) (*8*). A combination of sea-floor morphology, nephelometer data, and sedimentary evidence (*9*) was used to infer the location of the WBUC in a region where bottom current meters indicated a bottom current with a velocity as high as 72 cm/sec at a depth of 4988 m (*10*). The upper limit of the high-velocity current is placed at approximately 4500 m (*9*) on the basis of the most shallow occurrence of medium-scale (10-cm) ripples. Small-scale (< 10 cm) ripples were observed on the rise at depths of 4000 to 4500 m (*9*). The results of the HEBBLE study and earlier results indicate that the WBUC resides on the continental slope and rise but apparently has a high-velocity region at depths below 4000 m.

In addition to contourite deposition by the WBUC, other mechanisms may affect deposition on the continental slope and rise. Turbidity currents and shelf-slope spillover may deposit sediment derived from more shallow sources (*11*). Since turbidites are deposited by a down-slope current whereas contourites are deposited by an along-slope current, the direction of transport, as revealed by grain alignment, has been proposed as a means to delineate the two modes (*12*). The assumption of grain alignment parallel to turbidity-current flow (*12*), however, has been challenged by more recent work which shows that grains near the base of a turbidite may be aligned normal to the current as a result of traction transport along the bottom during deposition (*13*). Turbidites on the slope may be restricted to submarine canyons and adjacent spillover areas (*14*). Therefore, we have restricted our study on the slope to intercanyon areas in order to reduce the possibility of encountering turbidites and slump deposits (*15*). Below 4300 m, however, the canyons lose topographic expression, and areas of localized turbidite deposition are difficult to predict.

To our knowledge, none of the earlier investigators of sediments beneath the WBUC (*4–7, 9*) have used parameters that are sensitive to modern benthic oceanography and applicable to relative paleovelocity or paleoposition estimates for the WBUC. We have measured two sedimentological parameters in gravity core-top samples (*16*) from a study area on the continental slope and rise from New Jersey to North Carolina (Fig. 1). These two parameters have been shown to be sensitive to relative bottom-current velocity in deep-sea sediments (*13, 17*); the carbonate-free mean silt size (*18*) and magnetic grain long-axis alignment efficiency (*19*) are independent methods used to identify the location of high-velocity, deep-sea bottom currents.

Figure 2 shows the cross section of

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