for studies of hot spots—regions on the earth's surface of intense intraplate volcanism.

CHARLES R. CARRIGAN*
Department of Earth Sciences, Bullard Laboratories, Cambridge University, Cambridge, England, and
Geophysical Research Division, Sandia National Laboratories, Albuquerque, New Mexico 87115

References and Notes

1. Convection below 700 km is not necessarily ruled out by this model since independent circulation systems could exist in the upper and lower mantle.
2. L. Knopoff, *Geophys. Monogr. Am. Geophys. Union 13* (1969), pp. 683–689; D. J. Stevenson and J. S. Turner, in *Earth, Its Origin, Evolution and Structure*, M. McElhinny, Ed. (Academic Press, New York, 1979), pp. 227–263.
3. F. H. Busse and N. Riahi, *J. Fluid Mech.* **96**, 243 (1980).
4. J. M. Hewitt, D. P. McKenzie, N. O. Weiss, *Earth Planet. Sci. Lett.* **51**, 370 (1980).
5. M. M. Chen and J. Whitehead, *J. Fluid Mech.* **31**, 1 (1968).
6. The symbols α, g, H, d, C_p, ν, κ, and ρ are, respectively, the volumetric coefficient of thermal expansion (4×10^{-5} K^{-1}), the earth's gravitational acceleration (981 cm/sec^2), the volumetric heating rate (1.6×10^{-16} cal/cm^3-sec), the depth of the convection layer (6×10^7 cm), the specific heat (0.3 cal/g-K), the kinematic viscosity (10^{20} cm^2/sec), the thermal diffusivity (4×10^{-3} cm^2/sec), and the density (4 g/cm^3). The numbers are appropriate for the values of these parameters in the mantle.
7. P. H. Roberts, *J. Fluid Mech.* **30**, 33 (1967).
8. R. Krishnamurti and L. N. Howard, *Proc. Natl. Acad. Sci. U.S.A.* **78**, 1981 (1981).
9. The Biot number based on the thickness of the thermal boundary layer is of order unity or less.
10. F. M. Richter and B. Parsons, *J. Geophys. Res.* **80**, 2529 (1975).
11. I thank D. P. McKenzie for his suggestions and for providing support, financial and otherwise, during the laboratory phase of this study, which was carried out at Cambridge University, and D. Gubbins and J. A. Jacobs for helping to make possible my visit there. A United Kingdom Natural Environment Research Council grant and an NSF-administered NATO fellowship funded the work at Cambridge University. The work at Sandia National Laboratories was supported under DOE contract DE-AC04-76-DP00789.

* Send reprint requests to Sandia National Laboratories, Albuquerque, N.M. 87115.

8 May 1981; revised 21 September 1981

Slowly Dechlorinated Organic Chloramines

Abstract. *Dechlorination of some organic chloramines with aqueous sulfite solutions does not take place instantaneously as previously assumed. Field dechlorination times on the order of hours for some compounds that are found in chlorinated effluents appear likely on the basis of laboratory studies. These chlorinated compounds are not detected by standard analytical methods in the presence of sulfite ion.*

Chlorinated effluents from electric power plants or sewage treatment plants have the potential to adversely affect the aquatic biota of the receiving water body (*1*). One approach to the control of chlorinated effluents is the use of chemical dechlorination, which usually consists of the addition of sulfur dioxide or sodium bisulfite ($NaHSO_3$) to the effluent to degrade the oxidizing chlorine species to chloride ion. The conventional wisdom has held that, provided proper mixing is achieved, the reaction is quantitative and virtually instantaneous (*2*). We have found that at least some of the organic chloramines that form in chlorinated effluents react relatively slowly with aqueous SO_3^{2-} under environmentally meaningful conditions. Furthermore, with the present analytical techniques it is not possible to detect these compounds in the presence of excess unreacted dechlorinating agent. The extent and environmental significance of these slowly reacting compounds is presently unclear.

A significant proportion of the nitrogen compounds in many chlorinated effluents contain amino nitrogen groups. They are found in the *N*-terminal groups of amino acids and peptides, the amine nitrogens of peptides, and the alkyl amine groups in the side chains of such amino acids as lysine (*3*). The *N*-terminal amino groups and the alkyl amines readily react with hypochlorous acid (HOCl), formed by the hydrolysis of chlorine gas or sodium hypochlorite (NaOCl), to give chloramines (*4*). In the course of studies of the reaction chemistry of these compounds, we found that at concentrations expected to be found in effluents ($\sim 10^{-5}M$), the reaction

$$RNHCl + HSO_3^- + H_2O \rightarrow RNH_2 + SO_4^{2-} + Cl^- + 2H^+ \quad (1)$$

is relatively slow (R is an organic molecular fragment).

We have investigated the kinetics of Eq. 1, using several different organic chloramines at 25°C. We followed the reactions by taking periodic aliquots of the reaction mixture and analyzing them according to the fluorescamine fluorometric method (*5*) to measure the concentration of the primary amines formed by the reaction of the chloramines with the aqueous SO_3^{2-}. This procedure is based on our observation that chloramines do not react with the fluorescamine reagent to form a fluorescent product. The fluorescence was measured with a fluorometer (Turner model 111). The reactions were carried out under conditions of excess SO_3^{2-} so that the reaction would obey pseudo–first-order kinetics. The monochloramine in all cases was formed by the reaction of the amine with an equimolar solution of NaOCl at concentrations of 3 to 11 μM for 5 minutes. Sodium sulfite was then added to achieve an initial molar ratio to chloramine of from 3:1 to 30:1 in the reaction mixture. The pH was controlled with $0.02M$ phosphate buffers, and the temperature was regulated to ± 0.1°C.

If Eq. 1 is first order in the chloramine and in total SO_3^{2-}, the rate of appearance of the amine can be described by the equation

$$\frac{d[A]}{dt} = k[S]\,[CLA] \quad (2)$$

where $[A]$ is the concentration of the amine (in moles per liter), $[S]$ is the concentration of total SO_3^{2-}, $[CLA]$ is the concentration of chloramine, and k is the rate constant (in liters per mole per minute). The solution of Eq. 2 under the assumptions of constant $[S]$ and $[CLA]_0 = [A]_t$ is

$$1 - \frac{[A]}{[A]_t} = \exp(-k[S]t) \quad (3)$$

where $[CLA]_0$ is the initial concentration of chloramine and $[A]_t$ is the sum of concentrations of chloramine and free amine. The pseudo–first-order rate constant ($k' = k[S]$) can then be calculated using the method of least squares to fit the data on $\ln(1 - [A]/[A]_0)$ versus time. We determined k' in this way for varying conditions of $[A]_0$, $[S]$, and pH for the chloramine *N*-chloroalanylalanylalanine. The results showed that k' is independent of $[A]_0$ and varies linearly with $[S]$. These results confirm the assumption that Eq. 1 is first order in $[CLA]$ and $[S]$. The second-order rate constant is then obtained by dividing k' by $[S]$. Figure 1

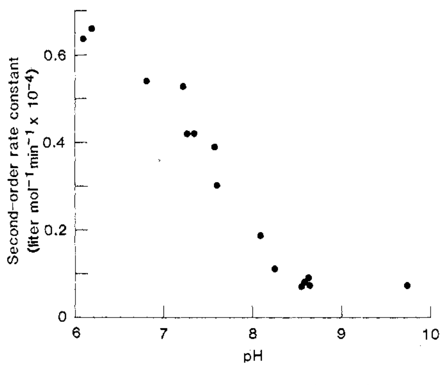

Fig. 1. Second-order rate constant of the reaction of *N*-chloroalanylalanylalanine at 25°C as a function of pH.

summarizes the results of these calculations as a function of pH. The shape of this curve and the location of the inflection point suggest that the pH 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 $\times 10^{-4}$) for several representative organic chloramines at pH 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 pH 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.

WILLIAM D. STANBRO
MICHAEL J. LENKEVICH
Applied Physics Laboratory,
Johns Hopkins University,
Laurel, Maryland 20707

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.

24 September 1981; revised 10 November 1981

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 pH 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