In summary, the two species curves developed in this study (Fig. 1) clearly demonstrate the advantages of monospecific samples for: (i) eliminating the errors (scatter) generated by the variability in foraminiferal assemblages, and (ii) providing a high degree of dating precision through rapidly epimerizing species, for example *G. tumida* (50,000 to 400,000 year range). If intercore correlations now being studied are successful, the *G. tumida* curve for V28-238 (Fig. 1) could be used as an empirical calibration curve for dating marine sediments at any location. Species curves, with their minimal scatter and linear segmented nature, provide a promising basis for future empirical and modeling studies of isoleucine epimerization in deep-sea sediments.

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References and Notes

1. The term epimerization is used in this report, rather than racemization, to describe the configurational change from L-isoleucine to D-alloisoleucine. Epimerization is the preferred term for conversions involving compounds, such as isoleucine, with two asymmetric carbon atoms.
2. P. E. Hare and R. M. Mitterer, *Carnegie Inst. Washington Yearb.* **67**, 205 (1969).
3. ______, *ibid.* **65**, 362 (1967).
4. P. E. Hare and P. H. Abelson, *ibid.* **66**, 526 (1968).
5. K. A. Kvenvolden, E. Peterson, F. S. Brown, *Science* **169**, 1079 (1970).
6. J. L. Bada, B. P. Luyendyk, J. B. Maynard, *ibid.* **170**, 730 (1970).
7. J. Wehmiller and P. E. Hare, *ibid.* **173**, 907 (1971).
8. J. L. Bada and R. A. Schroeder, *Earth Planet. Sci. Lett.* **15**, 1 (1972).
9. K. King, Jr., and P. E. Hare, *Carnegie Inst. Washington Yearb.* **71**, 596 (1972).
10. K. A. Kvenvolden, E. Peterson, J. Wehmiller, P. E. Hare, *Geochim. Cosmochim. Acta* **37**, 2215 (1973).
11. K. King, Jr., and P. E. Hare, *Science* **175**, 1461 (1972).
12. Data on isoleucine epimerization in marine sediments have been largely interpreted in terms of a reversible first-order kinetic model. A linear relationship between log $[(X_e - X)/X_e]$ and sediment age indicates a reversible first-order mechanism according to the approach of Wehmiller and Hare (*7*). X_e is the value of alloisoleucine/(alloisoleucine + isoleucine) at equilibrium, and X is the value of this ratio at time t.
13. K. King, Jr., and P. E. Hare, *Micropaleontology* **18**, 285 (1972).
14. R. M. Mitterer, in *Advances in Organic Geochemistry: 1971*, H. R. von Gaertner and H. Wehner, Eds. (Pergamon, Elmsford, N.Y., 1972), p. 441.
15. N. J. Shackleton and N. D. Opdyke, *J. Quat. Res.* **3**, 39 (1973).
16. N. J. Shackleton, personal communication.
17. G. B. Dalrymple, in *Calibration of Hominoid Evolution*, W. W. Bishop and J. A. Miller, Eds. (Scottish Academic Press, Edinburgh, 1972), p. 107.
18. A. W. H. Bé, in *Fiches Ident. Zooplancton*, No. 108 (1967).
19. W. H. Berger, *Deep-Sea Res.* **15**, 31 (1968).
20. This equilibrium alloisoleucine/isoleucine ratio of 1.40 is based on previously reported values for Middle Miocene *Mercenaria* (*3*) and Lower Paleocene planktonic foraminifera (*7*).
21. J. Imbrie and N. G. Kipp, in *Late Cenozoic Glacial Ages*, K. K. Turekian, Ed. (Yale Univ. Press, New Haven, 1971), p. 71.
22. W. H. Berger, *J. Foraminiferal Res.* **3**, 187 (1973).
23. These faunal changes may approximate a minimum response, since this Caribbean core (water depth 2730 m) reflects a relatively narrow range of paleoclimatic variations and a minimal degree of carbonate dissolution (*20*).
24. We thank J. D. Hays, N. D. Opdyke, N. J. Shackleton, and J. F. Wehmiller for their helpful comments on the manuscript. The technical assistance of P. Manley is gratefully acknowledged. Supported by National Science Foundation grants DES72-01571, DES75-18136, IDOE GX 28671, and a Columbia University faculty fellowship to C.N. Contribution No. 2478 of the Lamont-Doherty Geological Observatory.

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Sunlight-Induced Bromate Formation in Chlorinated Seawater

Abstract. *Chlorinated waters are being introduced into estuarine and coastal areas in increasing quantities. In such systems, the chlorine reacts with the natural bromide and ammonia to produce the highly toxic hypobromous acid, hypobromite ion, and haloamines. Sunlight causes up to 50 percent conversion to bromate ion, which is persistent in natural waters and has an unknown toxicity.*

Chlorine and its compounds have been used for water disinfection and as general aqueous biocides in increasing quantities since the turn of the century. The popularity of these materials stems partly from the remarkable apparent tolerance of mammals to them (*1*) at concentrations that produce mortality of organisms ranging from bacteria to fish; that is, it kills them, not us. Recent estimates (*2*) indicate that more than 100,000 tons of chlorine are used annually for the partial disinfection of effluents from wastewater treatment plants, and such use may be expected to increase substantially as the secondary treatment systems mandated by Congress in Public Law 92–500 begin operation. An additional major use of these compounds is as antifouling agents in the cooling waters of electric generating plants. Somewhat more chlorine is used for this purpose than for wastewater treatment, based on a cooling water flow of 300,000 cubic feet per second (8400 m^3/sec) (*3*) and a dose of 0.5 mg of Cl_2 per liter.

The release of chlorinated waters is producing effects that are slowly being better documented as a result of continuing research. Summaries of current knowledge (*4*) show avoidance behavior and reproductive failure in many freshwater invertebrates and fish at chlorine concentrations of 0.003 to 0.005 mg/liter. Federal and state regulations have been based on measurements of "residual chlorine" for both control of wastewater treatment (in the state of Virginia, chlorine is added until the concentration in effluent is 2.0 mg/liter) and effluent limitations on power plants. Considering the strong sensitivity of aquatic organisms to "residual chlorine" and the present levels of chlorine use, substantial damage to aquatic resources may occur. For example, the present releases of chlorine to Chesapeake Bay and its tributaries would sterilize the whole system if there were not environmental degradation of the added chlorine. However, transformation of chlorine to persistent, but less acutely toxic, compounds may be hypothesized to produce slow changes in the abundance and diversity of aquatic species in such situations.

Degradation is operationally defined as the disappearance of the analytical signal for "residual chlorine." As pointed out by Eppley *et al.* (*8*), different analytical methods produce very different estimates of "residual chlorine." In fact, the products from chlorination of wastewaters and natural waters are a mixture of chlorine, hypochlorous acid, hypochlorite ion, inorganic and organic chloramines, and other compounds. A better term is "residual oxidants," and we use this in the remainder of this report.

Since a large fraction of the U.S. population resides in coastal areas, much of the chlorine is discharged to saline natural waters. There is an extensive literature (*4*) on chlorination of freshwater systems, but coastal and estuarine waters have not been studied extensively. Research programs are under way at several federal and university marine laboratories to alleviate this situation. The work on freshwaters, unfortunately, does not have much application to marine environments, because seawater has a bromide ion concentration of 65 mg/liter and the added chlorine reacts with it to produce hypobromous acid and hypobromite ion. Bromamines and chloramines may be formed in the presence of ammonium ion (*5*).

For normal seawater of pH 8, the initial products of chlorination are a mixture of hypobromous acid and hypobromite ion. Both of these compounds are unstable with respect to decomposition and disproportionation.

$$2HOBr \rightarrow 2H^+ + 2Br^- + O_2; \quad 2OBr^- \rightarrow 2Br^- + O_2 \tag{1}$$

$$3HOBr \rightarrow 3H^+ + 2Br^- + BrO_3; \quad 3OBr^- \rightarrow 2Br^- + BrO_3 \tag{2}$$

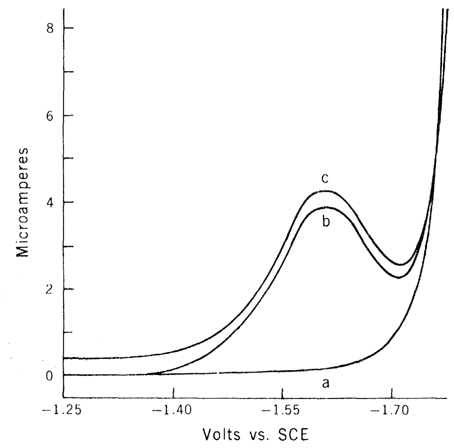

Fig. 1. Differential pulse polarographic verification of sunlight-induced bromate production in chlorinated seawater. (Curve a) Polarogram from untreated seawater, seawater immediately after chlorination to 4.9 ppm, or chlorinated seawater kept in the dark for 4 hours at 40°C. (Curve b) Polarogram from chlorinated seawater exposed to full sunlight for 70 minutes. (Curve c) Standard: 1.0 × $10^{-5}M$ sodium bromate in seawater, offset with respect to curves a and b. Polarograms were recorded at 25°C and *p*H 8.35; *SCE*, saturated calomel electrode.

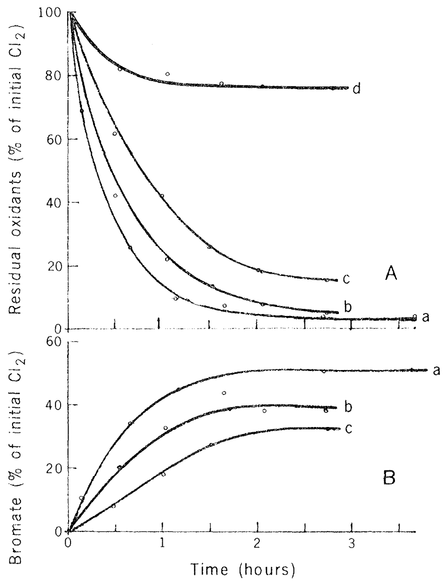

Fig. 2. (A) Disappearance with time of residual oxidants and (B) concomitant appearance of bromate (Eq. 2) in chlorinated seawater (4.2 to 4.9 ppm of Cl_2) as a function of exposure to sunlight. The conditions were: (curve a) full midday sunlight, (curve b) 65 percent of full sunlight, and (curve c) overcast, 20 percent of full sunlight. Curve d shows residual oxidant disappearance in the dark at 40°C. No bromate production was observed in the dark.

The rates of these reactions have not been measured in seawater. The decomposition of HOBr-OBr^- solutions has been considered most recently by Lewin and Avrahami (*6*) and by Engel *et al.* (*7*). Both groups conclude that the decomposition is to bromate plus bromide, with the disappearance of HOBr-OBr^- following second-order kinetics. The rate constant for this disappearance is shown to increase slightly with increasing HOBr-OBr^- or bromide ion concentration and to decrease strongly with increasing *p*H (*7*). It is observed to be independent of the chloride ion concentration up to 0.5*M* (*6*). No photolytic effects were investigated.

Previous investigators (*4, 8*) considered only the rates of disappearance of residual oxidants in chlorinated seawater and did not identify the products. The initial rapid decline was ascribed to reactions with organic compounds and the ensuing slower decline to "decomposition." No attention was given to photolysis by laboratory lighting or, more important, by natural sunlight. We report here our observations of residual oxidant disappearance and bromate formation, with particular reference to the significance of photolysis.

Chlorinated seawater was exposed to sunlight in open beakers placed in a bath of running seawater. In each experiment, six 400-ml beakers, each containing 300 ml of filtered (Millipore, 0.22 μm) Florida Current water, were placed in a bath. After temperature equilibrium was reached, sufficient NaOCl solution (buffered to *p*H 8.1 with Na_2CO_3) was added to each beaker to give an initial OCl^- normality equivalent to approximately 4.5 mg of Cl_2 per liter. Actual initial OCl^- concentrations varied somewhat (4.2 to 4.9 mg of Cl_2 per liter) among experiments because of varying OCl^- concentrations in the stock solution. Florida Current water contains less than 1 μM NH_3, so formation of haloamines cannot take up more than ~ 5 percent of the added Cl_2.

Light intensities were estimated with a Yellow Springs Instrument–Kettering model 65A radiometer, operated with the focusing head removed from the sensing element. This made it possible to measure relative light intensities from day to day without the extreme angular dependence caused by the focusing head. Experiments were conducted under full sun, partial sun, and heavily overcast conditions.

After chlorination, beakers were removed from the sunlight at regular (usually 30-minute) intervals, placed in a dark box, and analyzed for bromate and residual oxidants without delay. Residual oxidants analyses were performed by the I_3^- spectrophotometric titration procedure described by Carpenter (*10*) with a *p*H of 2 and a KI concentration of 4 g/liter. Bromate analyses were made by differential pulse polarography at 25°C and a *p*H of 8.35 (after O_2 stripping with N_2), using a Princeton Applied Research model 174A polarographic analyzer.

A typical polarographic recording is shown in Fig. 1. Curve a is the polarogram obtained for chlorinated seawater analyzed immediately after chlorination. Identical traces were observed for nonchlorinated seawater and for chlorinated seawater kept in the dark for periods up to 24 hours at temperatures up to 40°C, which indicates a lack of bromate formation under these conditions ($BrO_3^- \leq 10^{-7}M$, less than 0.5 percent conversion of Cl_2). Addition of copper sulfate to give a Cu^{2+} concentration in the seawater of 100 parts per billion did not induce measurable bromate production in the dark. Curve b was obtained from a chlorinated [4.9 parts per million (ppm)] seawater solution that was exposed to full sunlight for 70 minutes. Curve c, which is offset by 0.4 μa with respect to curves a and b, shows 1.0 × $10^{-5}M$ sodium bromate in seawater.

Figure 2 illustrates kinetic data for the appearance of bromate (Fig. 2A) and disappearance of residual oxidants (Fig. 2B) in chlorinated seawater exposed to sunlight. Curves a were obtained from solutions exposed to full midday sunlight for the duration of the experiment; curves b are for exposure to partial sunlight (the average light intensity was approximately 65 percent of full sunlight); and curves c are for overcast conditions (average light intensity, 20 percent of full sunlight). Curve d in Fig. 2A shows the disappearance of residual oxidants with time at 40°C in the dark. The ordinates are calibrated as the percentage of the added chlorine recovered as residual oxidants (Fig. 2A) or as bromate formed according to Eq. 2 (Fig. 2B).

The lack of observable bromate production in the dark is not inconsistent with the report of Lewin and Avrahami (*6*) that substantial bromate was formed in their 0.05*M* hypobromite solutions. Our solutions, which correspond to current chlorine use, were 1000 times more dilute. Using their rate constants, we calculate in our solutions a conversion to bromate of less than 1 percent after 24 hours.

The loss of residual oxidants does not correspond exclusively to bromate formation, and other reactions, including oxidation of organic matter and perhaps those in Eq. 1, also take place. The rate and extent of bromate formation depend on the intensity of sunlight.

Solutions of $10^{-5}M$ sodium bromate in seawater were also titrated by using the residual oxidants procedure. The results show that only about 5 percent of the added bromate appears as residual oxidants. Thus, the apparent residual oxidants remaining after exposure to sunlight could be completely due to bromate.

In another experiment, $1.0 \times 10^{-5}M$ solutions of sodium bromate in seawater were exposed to full midday sunlight for periods up to 4 hours and the residual oxidant and bromate concentrations were monitored. No measurable decline in bromate concentration or increase in residual oxidant was found.

Thus, the production of substantial amounts of bromate ion will cause erroneous results when standard analytical procedures are used for residual oxidants, especially procedures involving reaction of the oxidants with iodide ion. Bromate reacts sluggishly with iodide ion and the rate is dependent on factors such as reactant concentrations, *p*H, temperature, light, and content of transition metals. More important, it appears that large amounts of bromate have already been produced in estuarine and coastal waters with unknown effects. Extremely limited information is available on the direct toxicity of bromate ion (*4*). Further, the formation of bromate may provide a persistent source of low levels of known toxicants (such as hypobromite and bromamines) and brominated organics through the reverse of the formation reactions. In summary, present knowledge is totally inadequate to assess the environmental impacts of our discharge of chlorine to saline waters.

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References and Notes

1. C. J. Blabaum and M. S. Nichols, *J. Am. Water Works. Assoc.* **4B**, 1503 (1956).
2. R. L. Jolley, *Oak Ridge Natl. Lab. Tech. Memo.* (1973).
3. Federal Power Commission, *The 1970 National Power Survey* (Government Printing Office, Washington, D.C., 1971), part 1.
4. Environmental Studies Board, National Academy of Sciences–National Academy of Engineering, *Water Quality Criteria 1972* (Government Printing Office Washington, D.C., 1972); W. A. Brungs, *J. Water Pollut. Control Fed.* **45**, 2180 (1973); R. L. Jolley, in *Proceedings of a Conference on the Environmental Impact of Water Chlorination* (CONF-751096, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976).
5. J. D. Johnson and R. Overby, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **97**, 8425 (1971).
6. M. Lewin and M. Avrahami, *J. Am. Chem. Soc.* **77**, 4491 (1955).
7. P. Engel, A. Oplatka, B. Perlmutter-Hayman, *ibid.* **76**, 2010 (1954).
8. R. W. Eppley, E. H. Renger, P. M. Williams, *Estuarine Coastal Mar. Sci.* **4**, 147 (1976).
9. A. J. Downs and C. J. Adams, in *Comprehensive Inorganic Chemistry*, A. F. Trotman-Dickenson, Ed. (Pergamon, Oxford, 1973), vol. 2, p. 1404.
10. J. H. Carpenter, *Limnol. Oceanogr.* **10**, 135 (1965).
11. Supported by the Environmental Protection Agency and the Energy Research and Development Administration. D.L.M. was supported by an NSF Faculty Science Fellowship.

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Environmental Degradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

Abstract. *Herbicide formulations containing known amounts of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and exposed to natural sunlight on leaves, soil, or glass plates lost most or all of the TCDD during a single day, due principally to photochemical dechlorination. Despite the known persistence of pure TCDD, it is not stable as a contaminant in thin herbicide films exposed to outdoor light.*

The realization that pesticides and other chemicals derived from 2,4,5-trichlorophenol could contain the highly toxic and teratogenic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has caused more than 7 years of continuing public anxiety. More than 4×10^7 kg of Agent Orange (more correctly, Herbicide Orange) defoliant (*1*), representing a mean of more than 1.9 and a maximum of 47 parts per million (ppm, mg/kg) of TCDD, was sprayed over jungle in Southeast Asia (*2*), and a number of pesticides commonly used in the United States also were found to contain TCDD at ppm levels (*3*). However, despite the large-scale application of these materials, and extensive dioxin analysis and monitoring (*3*, *4*), there is little evidence of widespread occurrence of TCDD in the environment (*5*).

While pure TCDD is unstable toward ultraviolet light when dissolved in organic solvents such as methanol or benzene (*6*), it otherwise has the reputation of being very stable and persistent (*7*). However, opportunities for it to occur environmentally in pure form are negligible; its more probable behavior as a trace contaminant dissolved in pesticide mixtures would seem to have much more significance but, remarkably, has not been reported.

Thin films of pure TCDD on glass plates previously were found to be stable to sunlight for at least 14 days (*6*). In order to compare its stability in a formulation, thin layers (5 mg/cm^2) of Agent Orange containing 15 ppm of TCDD were exposed in borosilicate glass petri dishes to summer sunlight in Davis, California. The irradiated mixtures were subjected to alkaline hydrolysis, and the benzene-extracted TCDD was determined by gas-liquid chromatography (GLC) (*8*). Identical treatments, masked from sunlight, served as dark controls. Loss of the dioxin was rapid in sunlight (Fig. 1), and less than half remained after 6 hours.

The same Agent Orange also was applied evenly in droplets over excised leaves of a rubber plant (*Hevea brasiliensis*) (6.7 mg/cm^2) and on the surface of sieved Sacramento loam soil (10 mg/cm^2) and exposed to sunlight. TCDD was lost even more rapidly from the illuminated leaf surface than from glass (Fig. 2), while loss from soil was somewhat slower, presumably because of shading of lower layers by soil particles.

When a commercial Esteron brushkiller (*9*) containing TCDD (10 ppm) was exposed to sunlight in the glass dishes (5 mg/cm^2), the TCDD was lost at about the same rate as in the Agent Orange (Fig. 1) (*10*). However, when the Esteron formulation mixture, without any herbicides but containing TCDD at 10 ppm, was exposed to sunlight, the dioxin disappeared almost completely within 2 days. Analytical difficulties precluded further experiments with Esteron.

The disappearance of TCDD could be due to any of four factors: volatilization, absorption, mechanical loss, or photodecomposition. Pure TCDD does not volatilize appreciably from either a glass surface or a leaf under ambient conditions (*7*); however, if volatilization from a thin pesticide film were important, significant losses from the controls held in the dark at approximately the same temperature should have been observed. Impaired extraction due to sequestration in leaves or soil should not have permitted the efficient recoveries of TCDD from controls, and unforeseen mechanical losses are precluded for the same reason. Isensee and Jones (*11*) reported more than 90 percent recovery of pure TCDD from soybean leaves after more than 48 hours but assumed what loss there was to be due to volatilization, whereas it actually may have been due to photodecomposition.