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.

Donald L. Macalady[*]
James H. Carpenter
Cynthia A. Moore
Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149

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[*] Present address: Department of Chemistry, Northern Michigan University, Marquette 49855.

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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*).

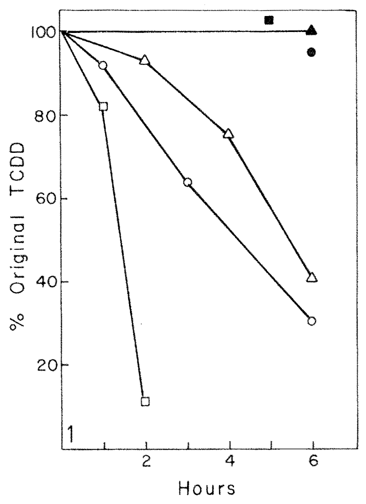
While pure TCDD is unstable toward ultraviolet light when dissolved in organic solvents such as methanol or benzene (*6*), it otherwise has the reputation of being very stable and persistent (*7*). However, opportunities for it to occur environmentally in pure form are negligible; its more probable behavior 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.



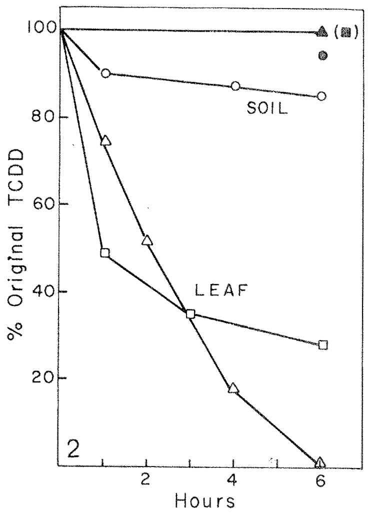


Fig. 1 (left). Loss of TCDD from formulations on glass surfaces. Esteron (○), Esteron formulating agents (□), and Agent Orange (△). Points connected only to aid distinction. Closed symbols are dark controls. Fig. 2 (right). Loss of TCDD from Agent Orange on leaves at 6.7 mg/cm^2 (△), at 1.3 mg/cm^2 (□), and on soil (○). Closed symbols are dark controls.

Our measurements indicate that sunlight is the principal factor in dioxin disappearance from inert surfaces, plants, and soils treated with TCDD-contaminated pesticides. In every experiment, light caused the TCDD content to decline sharply, while dark controls remained virtually unaffected. The detection by mass spectrometry (*12*) of traces of dichloro- and trichlorodibenzo-*p*-dioxins in each pesticide after several hours of exposure to sunlight on glass surfaces (but not in the dark) and similar detection of the characteristic mass spectrum of the trichlorodibenzo-*p*-dioxin in extracts from coated leaves exposed to sunlight offer further evidence of dioxin destruction by photochemical dechlorination (*6, 13*). They also differentiate the dioxins from known chlorinated interferences such as bis(2,4-dichlorophenoxy)methane (*14*). Although light absorption by the herbicide slows the photodecomposition rate significantly compared to that in formulating agents without herbicide, a sufficient window exists in its spectrum to allow light absorption above 300 nm by TCDD (Fig. 3).

Photodegradation of the herbicide formulation on soil under conditions where pure TCDD remained unchanged (*6*) emphasizes what we view as the three requirements for significant dioxin breakdown: dissolution in a light-transmitting film, the presence of an organic hydrogen-donor such as solvent or pesticide, and ultraviolet light. All three conditions normally should have been met consistently during the practical application or accidental loss of 2,4,5-T and other TCDD-containing chemicals such as trichlorophenol.

For analytical convenience, the initial levels of herbicide application in these experiments generally were much larger than those that have ever been used in practice (5 mg/cm^2 = 500 kg/ha), although the TCDD concentrations on which photolysis rates depend were representative of those that existed at one time (*7*). Any differences in degradation rate between different amounts of herbicide (Fig. 2) probably are due to daily variation in light intensity. Although no TCDD analyses appear to have been made during the period of heavy use of Agent Orange in Southeast Asia, and the present levels of TCDD in commercial pesticides result in field residues below normal detectability (*15*), our data strongly suggest that environmental residues of TCDD often will be considerably less than previously expected (*16*). They also suggest that TCDD might be removed from contaminated surfaces by treatment with a low-volatility solvent and ultraviolet light.

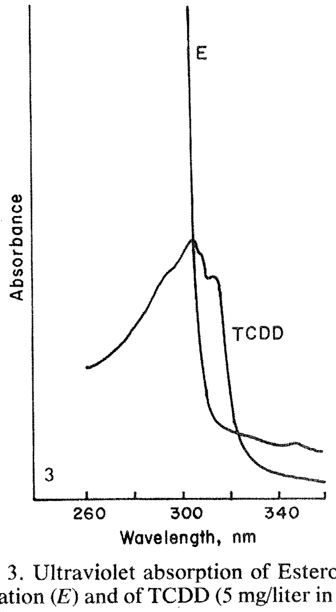


Fig. 3. Ultraviolet absorption of Esteron formulation (*E*) and of TCDD (5 mg/liter in methanol).

DONALD G. CROSBY
ANTHONY S. WONG
Department of Environmental Toxicology, University of California, Davis 95616

References and Notes

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8. The herbicide was extracted into benzene and the solvent was removed by evaporation. Residues were boiled with 10 percent aqueous sodium hydroxide solution, TCDD was extracted with benzene, and the dried and concentrated extract was analyzed on a glass GLC column containing 10 percent DC-200 on Gas-Chrom Q, 80/100 mesh, at 220°C. The Finnigan model 1015C mass spectrometer detector monitored the effluent at *m/e* (mass/charge) 320 and *m/e* 285; the total-ion response was linear at 1 to 50 ng and sensitive to 0.1 ng of TCDD. Gas chromatograms of Agent Orange were unexpectedly complex and showed considerable interference near the TCDD retention time.
9. Esteron contained 2,4,5-T propyleneglycol butyl ether ester (34.1 percent), 2,4-D propyleneglycol butyl ether ester (36.0 percent), and diesel oil No. 2 plus nonionic emulsifier (29.9 percent).
10. Esteron samples were extracted into benzene-hexane (1 : 10), passed through a column of freshly activated alumina with a precolumn layer of anhydrous sodium sulfate, eluted with benzene preceded by hexane and ether-hexane (1 : 10), and TCDD was analyzed by GLC on a glass column containing 5 percent SE-30 on Chromasorb G (60/80 mesh) at 200°C with an electron capture detector. Recovery of standards from glass plates was 95 percent, but the emulsifiers caused considerable difficulty with other analyses.
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12. Characteristic mass spectra showing molecular ion (M^+) *m/e* 252 with a Cl_2 isotope cluster and M^+ *m/e* 286 with a Cl_3 cluster identified di- and trichlorodibenzo-*p*-dioxin, respectively, but the levels were too low to measure accurately.
13. Photoreduction of similar chloro compounds has been described by D. G. Crosby and N. Hamadmad [*J. Agric. Food Chem.* **19**, 1171 (1971)] and S. Safe and O. Hutzinger [*Nature (London)* **232**, 641 (1971)].
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16. Authentic TCDD was supplied by J. H. Davidson, Agent Orange by E. P. Lira, and mass spectrometry assistance by P. A. Taylor and C. Reece. Supported in part by USDA Regional Research Project W-45. We thank the California Analytical Laboratories, Sacramento, for use of their mass spectrometer.

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