AAAS-Newcomb Cleveland Prize
To Be Awarded for a Report Published in *Science*

The AAAS-Newcomb Cleveland Prize, which previously honored research papers presented at AAAS annual meetings, is now awarded annually to the author of an outstanding paper published from September through August in the Reports section of *Science*. The second competition year under the new rules starts with the 2 September 1977 issue of *Science* and ends with that of 25 August 1978. The value of the prize is $5000; the winner also receives a bronze medal.

To be eligible, a paper must be a first-time publication of the author's own research. Reference to pertinent earlier work by the author may be included to give perspective.

Throughout the year, readers are invited to nominate papers appearing in the Reports section. Nominations must be typed, and the following information provided: the title of the paper, issue in which it was published, author's name, and a brief statement of justification for nomination. Nominations should be submitted to AAAS-Newcomb Cleveland Prize, AAAS, 1515 Massachusetts Avenue, NW, Washington, D.C. 20005. Final selection will rest with a panel of distinguished scientists appointed by the Board of Directors.

The award will be presented at a session of the annual meeting at which the winner will be invited to present a paper reviewing the field related to the prizewinning research. The review paper will subsequently be published in *Science*. In cases of multiple authorship, the prize will be divided equally between or among the authors; the senior author will be invited to speak at the annual meeting.

Reports

Phthalate Ester Plasticizers: A New Class of Marine Pollutant

Abstract. *Phthalate ester plasticizers have been detected in the open-ocean environment. Samples consisting of water, sediment, air, and biota from the Gulf of Mexico and of water and air from the North Atlantic were analyzed and found to contain two phthalate esters, di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-dibutyl phthalate (DBP); the concentrations of polychlorinated biphenyls (PCB's) and DDT's (*p,p'*-DDT and *p,p'*-DDE) were also determined. Like the ubiquitous PCB's and DDT's, the phthalate plasticizers were found in almost all samples analyzed; DEHP was present at higher concentrations than the PCB's or DDT's in water and sediment. The environmental impact of the concentrations found in these studies, coupled with the continued high production and wide use of these plasticizers, requires assessment.*

The use and production of phthalate ester plasticizers (PAE's) has been steadily increasing over the past two decades. The total annual production has reached nearly a 5×10^8 kg and continues to increase. The high rate of production of PAE's, coupled with their widespread use and some instances of toxicity to aquatic organisms (*1*), suggested to us that PAE's may be contaminating the marine environment on a large scale. A search for the more abundantly produced phthalate plasticizers, di-2-ethylhexyl phthalate (DEHP) and di-*n*-butyl phthalate (DBP), in marine water, sediment, air, and biota was therefore initiated. The results we obtained clearly show that PAE's are a new class of marine pollutant.

As far as we know, prior to this study, no systematic studies of the PAE's in the marine environment have been reported, although these materials have been detected in many environmental samples (*2*). One reason for the paucity of data from the marine environment is that suitable techniques for detecting the very low concentrations of phthalates expected in marine samples have been unavailable. The major deterrent to measurement of this ultralow content is the extreme difficulty in reducing background contamination to acceptable levels (in the case of water, below parts per trillion). One example of this difficulty in reducing contamination is a report by other workers that background values were 1500 ng of DEHP and 1000 ng of DBP in spite of precautions taken to minimize these values (*3*). For our studies of concentrations in the marine environment, background values of 50 ng of DEHP and 25 ng of DBP (or lower) were achieved (*4*). Recoveries of phthalates from spiked samples were typically 90 percent or better.

The techniques that we used for these analyses were based on extraction with suitable organic solvents, separations from other contaminants by column chromatography, identification and quantitation by gas chromatography with an electron capture detector (*4*), and confirmation by chemical derivatization (*5*). These techniques are suitable for the detection and quantitation of a number of the dialkyl phthalate esters, but only two esters, DEHP and DBP, were detected in the samples analyzed. Moreover, with this procedure it was possible to determine the ubiquitous polychlorinated biphenyls (PCB's) and DDT's (*p,p'*-DDT and *p,p'*-DDE) along with the phthalates. These chlorinated hydrocarbon pollutants are known to be present in almost all environmental samples (*6*); the data on the chlorinated hydrocarbons are given with those for the phthalates for purposes of comparison (Table 1). Typical background values for PCB's and DDT's are <1 ng and <1 pg, respectively.

Sediment samples were taken with metal-coring devices and preserved frozen in glass containers until analysis. The core sections analyzed represented surface sediment and were taken from the top 10 cm. In general, sediment values of PAE's, PCB's, and DDT's decreased from the Mississippi delta region to the open Gulf of Mexico.

We either extracted the organic compounds from the water samples directly or concentrated them at the collection site by drawing the sample through a bed of precleaned Amberlite XAD-2 resin.

Table 1. Mean concentrations and concentration ranges of DDT's, PCB's, and two phthalate plasticizers in the Gulf of Mexico (39°00'N, 70°40'W) and the northern Atlantic (38°00'N, 69°35'W); nd, none detected.

Sample	Number of samples	DDT's		PCB's*		DBP		DEHP	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
Surface water (nanograms per liter)									
Typical blank		<0.002		<0.02		<0.1		<0.2	
Mississippi delta	14	1.7	0.01–2.9	2.45	1.7–3.3	95	6.5–471	70	23–225
Gulf coast	10	0.35	0.01–0.6	1.60	0.1–3.1	74	3.4–265	130	6–316
Open gulf	7	0.25	<0.1–0.6	1.4	<0.1–2.8	93	3–133	80	6–97
North Atlantic†	10	nd	nd	0.16	0.02–0.20	nd	nd	4.9	0.1–6.3
Sediment (nanograms per gram)									
Typical blank		<0.002		<0.02		<0.1		<0.2	
Mississippi delta	22	4.2	0.2–9.3	18.7	0.2–35	13	<0.1–52.1	69	<0.1–248
Gulf coast	9	1.3	0.2–4.0	1.97	0.2–6	7.6	<0.1–15.3	6.6	3.4–14.2
Open gulf	3	0.23	0.1–0.5	0.2		3.4	1.6–5.6	2.0	
Air (nanograms per cubic meter)									
Typical blank		<0.0005		<0.03		<0.03		<0.4	
Gulf of Mexico	8	0.04	<0.02–0.09	0.4	0.27–0.91	0.3	0.08–0.7	0.4	<0.4–2.3
North Atlantic	5	0.006	0.002–0.014	0.46	0.1–0.94	1.0	0.4–2.3	2.9	1.4–4.1
Biota (nanograms per gram)									
Typical blank		<0.003		<0.02		<0.1		<0.2	
Gulf of Mexico‡	20	11.4	0.1–55	29.6	1–68	<0.1		4.5	<1–135

*Samples were compared to Aroclor 1260 or Aroclor 1254. †Part of a large intercalibration study (*13*). ‡Biota examined included fish, crabs, shrimp, eel, rays, a jellyfish, and a starfish.

The resin was then covered and transferred to the laboratory for elution and analysis. Average values (in nanograms per liter) for all water samples taken in the gulf were as follows: DEHP, 90; DBP, 80; PCB's, 2; and DDT's, 1. In general, higher concentrations of DEHP were found in the coastal regions than in the open gulf or in the Mississippi delta although the concentration ranges were quite large. For DEHP and DBP, relatively lower average values of 70 and 95 ng/liter, respectively, were found in the Mississippi delta area, whereas the concentrations of DDT's and PCB's (1.7 and 2.5 ng/liter, respectively) were higher in the delta region than in the other areas sampled. Sample concentrations from the North Atlantic were lower by roughly a factor of 10 than those observed in the gulf.

Biota samples (mainly fish) were obtained by hook and line or trawl and were stored frozen in glass jars or aluminum foil until analyzed. For larger fish, only muscle tissue—free of skin—or excised organs were analyzed; smaller organisms were analyzed whole. The only phthalate detected in the majority of these samples was DEHP. An average DEHP concentration of 5 ng/g was found, a low value relative to the average concentrations of 10 and 26 ng/g for DDT's and PCB's, respectively. In view of the higher water and sediment concentrations of DEHP, this finding indicates that the phthalates are either taken up more slowly or metabolized and excreted more rapidly than the chlorinated hydrocarbons. In those samples in which liver tissue was analyzed separately, the concentrations of DEHP in liver were lower than in muscle, whereas the reverse was found for DDT's and PCB's. This finding implies that metabolism is responsible for the low phthalate concentrations in biota (*7*).

We made atmospheric measurements over the Gulf of Mexico by drawing air through columns of Florisil (*8*) or polyurethane foam (*9*). The columns were then brought to the laboratory for elution and gas chromatographic analysis. The samples yielded the following mean concentrations (in nanograms per cubic meter): DEHP, 0.4; DBP, 0.3; PCB's, 0.4; and DDT's, 0.04. The atmospheric concentrations of PCB's and DDT's were similar to the values of 0.5 ng/m^3 for PCB's and 0.03 ng/m^3 for DDT's found in the atmosphere over the Sargasso Sea (*10*). Atmospheric samples taken in the North Atlantic showed generally lower DDT but higher PCB and DEHP concentrations.

The major environmental routes of DBP and DEHP to the gulf have not yet been established. Although the exact transfer pathways and mechanisms are not yet fully understood, it is apparent that significant amounts of phthalates are entering the marine environment.

Whereas the chlorinated hydrocarbons are generally used and dispersed as entities, the phthalates are almost exclusively incorporated into other matrices such as plastics before being used and dispersed. This use pattern, along with the high disposal rates of plastics, may be producing an environmental reservoir of the phthalates from which these compounds are slowly being leached. Such a reservoir has several important implications: the concentrations measured represent only a fraction of the phthalates in the environment, and environmental values would not decrease readily even if phthalate use were to be stopped. Even though the presence of the ester function may make the phthalates less persistent than the chlorinated hydrocarbons, the relatively high concentrations of phthalates found in these studies indicate that environmental accumulation is occurring.

The significance of the presence of phthalates, especially in the Gulf of Mexico, requires assessment. The toxicity of the phthalates to marine organisms has not been well documented, but it is under investigation. Studies with mammals have generally indicated a low order of acute toxicity (*2*); however, there have been a number of toxic effects reported from sublethal exposures. For example, a recent study indicates that DEHP affects lipid biosynthesis in rats (*11*). Of possibly greater importance to the marine environment are reports of reduced hatching success from brine shrimp eggs due to exposure to DBP (*12*) and of decreased reproductive rates in aquatic organisms caused by DEHP (*1*). The possibility of reproductive effects along with the high concentrations of DBP and DEHP in coastal areas where many marine species reproduce could cause an environmentally damaging disruption of marine food webs.

C. S. GIAM*, H.S. CHAN
G. S. NEFF, E. L. ATLAS
Chemistry Department, Texas A&M University, College Station 77843

References and Notes

1. F. L. Mayer, Jr., and H. O. Sanders, *Environ. Health Perspect.* **3**, 91 (1973); F. L. Mayer, Jr., D. L. Stalling, J. L. Johnson, *Nature (London)* **238**, 411 (1972).
2. J. Autian, *Environ. Health Perspect.* **3**, 3 (1973); S. P. Mathur, *J. Environ. Qual.* **3**, 189 (1974), and references therein.
3. D. T. Williams, *J. Agric. Food Chem.* **21**, 1128 (1973).
4. C. S. Giam, H. S. Chan, G. S. Neff, *Anal. Chem.* **47**, 2225 (1975).
5. C. S. Giam, H. S. Chan, T. Hammargren, G. S. Neff, D. L. Stalling, *ibid.* **48**, 78 (1976).
6. C. S. Giam, R. L. Richardson, M. K. Wong, A. R. Hanks, W. M. Sackett, *Bull. Environ. Contam. Toxicol.* **9**, 376 (1973); C. S. Giam, R. L. Richardson, D. Taylor, M. K. Wong, *ibid.* **11**, 189 (1974).
7. F. L. Mayer, *J. Fish. Res. Board Can.* **33**, 2610 (1976); D. L. Stalling, J. W. Hogan, J. L. Johnson, *Environ. Health Perspect.* **3**, 159 (1973).
8. C. S. Giam, H. S. Chan, G. S. Neff, *Anal. Chem.* **47**, 2319 (1975).
9. T. F. Bidleman and C. E. Olney, *Bull. Environ. Contam. Toxicol.* **11**, 442 (1974).
10. ———, *Science* **183**, 516 (1974).
11. F. D. Bell and D. J. Nazir, *Lipids* **11**, 216 (1975).
12. N. Sugawara, *Bull. Environ. Contam. Toxicol.* **12**, 421 (1974); *Toxicol. Appl. Pharmacol.* **30**, 87 (1974).
13. National Science Foundation Pollutant Transfer Intercalibration Study Participants, in preparation.
14. We thank J. K. Kakareka, T. F. Hammargren, and K. C. Hauck for expert technical assistance and associates of the Department of Oceanography, Texas A&M University, and Woods Hole Oceanographic Institute for assistance in obtaining samples. Supported by NSF grants OCE73-09743A04 and OCE76-14148.

* To whom all correspondence should be addressed.

18 April 1977; revised 1 August 1977

Chemical Etching of Fission Tracks in Polyfluoro Plastics

Abstract. *A method has been developed for the chemical etching of fission tracks in polyfluoro plastics. The formation of fine holes several tens of nanometers in diameter in polyvinylidene fluoride films, bombarded by fission fragments in oxygen and etched in 5-normal sodium hydroxide solution at 85°C, was confirmed by electron microscopy.*

The technique of chemical etching of charged particle tracks in plastic materials has been extended to polyfluoro plastics. We have obtained porous polyvinylidene fluoride films with fine holes several tens of nanometers in diameter by the chemical etching of fission tracks.

Plastics used widely in studies and applications of the chemical etching of tracks include polycarbonate, polyethylene terephthalate, and cellulose esters. We are interested in the chemical etching of tracks in substances having high chemical resistivity such as polyfluoro plastics since, from the viewpoint of scientific and technological applications, a membrane filter made by the etching of tracks in a chemically resistive substance will be extremely useful.

We have studied the chemical etching of tracks in polyvinylidene fluoride, because this film is the least porous and most impervious to gases of commercially available polyfluoro plastics, and is suitable for an examination of the growth of very fine holes. Polyvinylidene fluoride is a polymer known to have characteristics for radiation exposure intermediate between those of cross-linked polymers and degradation polymers. Makuuchi *et al.* and Seguchi *et al.* (*1*) studied the effects of γ- and β-rays on polyvinylidene fluoride and found that exposure to radiation in vacuum results in both cross-linking and chain scission with almost the same *G* value (the number of molecules changed per absorption of 100 ev of radiation energy) whereas exposure in air favors chain scission with a resultant decrease in the mean molecular weight. These investigators also measured the concentration of free radicals remaining after exposure of the polymer to radiation and found the lifetime of free radicals to be much longer than 24 hours. Accordingly, for the enhancement of the chemical etching of tracks in polyvinylidene fluoride, it appears that it would be effective to irradiate in oxygen or some other gas that reacts with active species formed in the cylindrical zone around the charged particle trajectories and to form chemical species of reduced molecular weight. On the basis of these considerations, we have bombarded fission fragments in oxygen and found a method for enlarging fission tracks in polyvinylidene fluoride films.

Polyvinylidene fluoride films 9 μm thick (Kureha Chemical Industries Co. Ltd.) were irradiated by fission fragments obtained from the thermal neutron fission of ^{235}U in reactor JRR-4 of the Japan Atomic Energy Research Institute. A natural uranium layer 100 nm thick deposited on an aluminum foil was used as a source of fission fragments. A collimator was disposed between the film and the fission source to obtain aligned tracks. The film, the fission source, and the collimator were contained in a quartz tube filled with oxygen and irradiated at a thermal neutron flux of 1.7×10^{13} cm^{-2} sec^{-1} for 10 minutes. The thickness of the film and of the uranium layer and the oxygen pressure were selected so as to satisfy the condition that all fission fragments entering the film have sufficient energy to penetrate the film. After cooling the film for several days to allow for the decay of fission products, we took the film out of the quartz tube and etched it in sodium hydroxide solution.

Figure 1a is a surface electron micrograph of a film irradiated in oxygen (pressure, 250 torr) and etched for 29 hours in 5*N* sodium hydroxide at 85°C. The electron micrograph was taken with a field emission scanning electron microscope (Japan Electron Optics Laboratory Co. Ltd., type JSM-F7). Holes about 50 nm

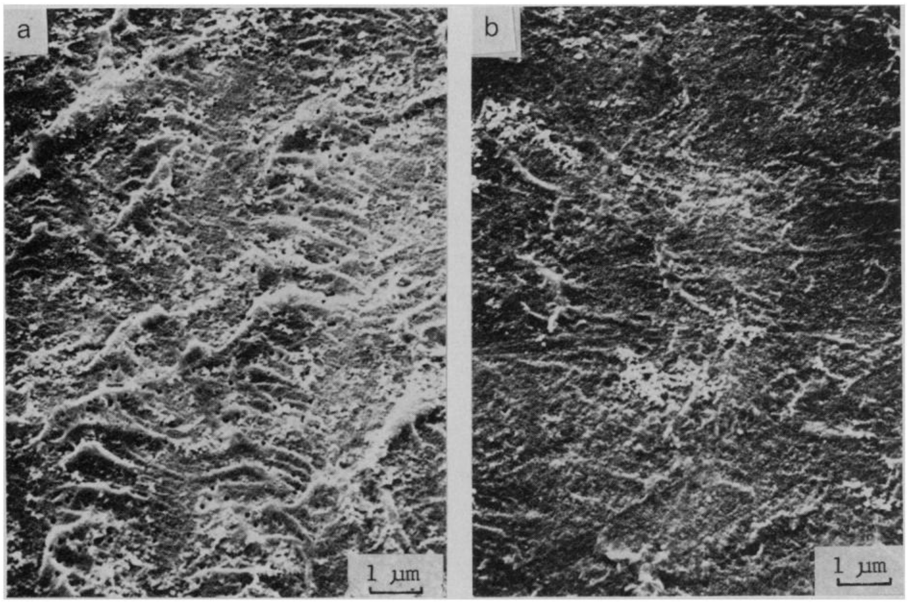

Fig. 1. Tracks of fission fragments in polyvinylidene fluoride film. Scanning electron micrographs of films irradiated in oxygen at a pressure of 250 torr (a) and in vacuum (b). Both were etched for 29 hours in 5*N* sodium hydroxide at 85°C. A gold-palladium alloy a few nanometers thick was deposited on the film.

0036-8075/78/0127-0421$00.50/0