Reports

Global Transport of Organic Pollutants: Ambient Concentrations in the Remote Marine Atmosphere

Abstract. *Concentrations of organic pollutants in the air and in precipitation have been measured at Enewetak Atoll in the North Pacific Ocean. These data from a site removed from industrial and human activity indicate the present concentrations of synthetic organic pollutants in the atmosphere and establish the long-range atmospheric transport of organic pollutants to remote marine areas. Hexachlorobenzene and hexachlorocyclohexane isomers are present in the remote marine atmosphere. Polychlorobiphenyls, total DDT, dieldrin, chlordane, and two phthalate ester plasticizers were also found in the samples. The concentrations of pollutants in the atmosphere remote from continental sources are good measures of the minimum concentrations of air pollutants on Earth.*

Recent studies have confirmed that the atmosphere is a significant pathway for the transfer of compounds from the continents to oceans (*1*-*6*). However, in most of the studies investigators have examined inorganic particulates including soil, minerals, and trace metals (*5*). Reports on atmospheric transfer of organics, especially anthropogenic or continental organics, are sparse and require different sampling techniques. Reports of chlorinated hydrocarbons, such as polychlorinated biphenyls (PCB's) and total DDT, and phthalate ester plasticizers in the atmospheres over the North Atlantic (*2*-*4*) and Gulf of Mexico (*1*, *2*, *6*) have demonstrated that organic pollutants are transported long distances in the atmosphere. These reports, together with studies of the atmospheres of remotely populated continental areas (*3*, *4*) and the Great Lakes region (*7*), indicate that some organic pollutants are being widely dispersed in the Northern Hemisphere. However, the data coverage is very limited in geographical extent. With the exception of some measurements of organic pollutants in Hawaiian rain (*8*), we are not aware of any reports of synthetic organics in the atmosphere over the Pacific Ocean. We summarize here the results of measurements of organic pollutants in air and rain samples taken during April through August 1979 at Enewetak Atoll in the North Pacific Ocean. Because of its remoteness from urban or manufacturing sources, pollutant concentrations measured at the site are not subject to episodal or local contamination. Thus, these measurements provide background data for selected organic pollutants against which future changes can be assessed. The sampling program was part of the Sea-Air Exchange (SEAREX) Program, a multidisciplinary project to evaluate the sources and fluxes of substances in the marine atmosphere.

Two sampling systems were used. In the high-volume system (450 to 500 liter/min) a glass-fiber filter backed by polyurethane foam was used to trap high-molecular-weight organic compounds (*9*, *10*). This system measures vapor-phase as well as particulate organics. The typical sample size was 1000 to 2000 m^3. In the low-volume system (20 liter/min) Florisil was used as the adsorbent. This system was used to trap volatile compounds not efficiently retained by polyurethane foam (*9*, *11*). The low-volume sample size is usually 75 to 150 m^3. After sampling, the adsorbents were extracted with appropriate solvents, separated by column chromatography, and analyzed by glass-capillary gas chromatography with electron capture detection. The confirmation of selected compounds, including phthalate esters, PCB's, hexachlorobenzene (HCB), α-hexachlorocyclohexane (α-HCH), and DDT, was performed by alkaline hydrolysis and gas chromatography-mass spectrometry. Rain was sampled in a 75-cm modified stainless steel funnel attached to a glass reservoir. Rain was collected during each shower and preserved with methylene chloride until analysis. Individual rain samples varied between 3 and 30 liters. Details of the sampling and analysis are given elsewhere (*9*, *11*-*13*). Because of the very low concentrations, strict precautions were taken to ensure contamination-free samples (*13*).

Samplers were mounted on an 18-m aluminum tower on an unpopulated island in the atoll (12°N, 162°E). Sampling was automatically controlled and occurred only if the wind speed exceeded 5 miles per hour, condensation nuclei counts were $< 500\ cm^{-3}$, and the wind direction was from 75° to 135°. The automatic system ensured that samples were representative of marine air. The ambient temperature ranged from 26° to 30°C.

Results of the analyses are presented in Table 1. Most compounds were found to pass through the glass-fiber filter (> 90 percent), and the results in Table 1 reflect only the vapor-phase concentrations. Rain samples were analyzed whole; thus the values represent total (dissolved and particulate) concentrations.

One of the major classes of organochlorine compounds measured was PCB's. These compounds were found primarily as the lighter isomers typical of the commercial mixture Aroclor 1242. With glass-capillary, temperature-programmed gas chromatography, we were able to identify at least 30 PCB ("fingerprint") isomers in the sample which matched those in Aroclor 1242 (Fig. 1). Heavier PCB's (Aroclor 1254) were estimated to be ~ 10 percent of the total PCB's present in the samples. Earlier

Table 1. Concentrations of some organic pollutants in the atmosphere and precipitation at Enewetak Atoll.

Compound	In air (ng/m^3)			In precipitation (ng/liter)		
	N	Mean	Range	*N*	Mean	Range
PCB Aroclor 1242	14	0.54	0.35 to 1.02	16	< 0.6	
Hexachlorobenzene	11	0.10	0.095 to 0.13	16	< 0.03	
α-Hexachlorocyclohexane	9	0.25	0.075 to 0.57	16	3.11	1.32 to 6.83
γ-Hexachlorocyclohexane	17	0.015	0.006 to 0.021	16	0.51	0.34 to 1.59
Chlordane (α and γ)	14	0.013	0.006 to 0.015	16	< 0.02	
Dieldrin	17	0.010	0.006 to 0.018	16	< 0.02	
p,*p*'-DDE	17	0.003	0.002 to 0.005	16	≤ 0.02	
Di-*n*-butyl phthalate	17	0.87	0.40 to 1.80	16	31	2.6 to 72.5
Di(2-ethylhexyl) phthalate	17	1.4	0.32 to 2.68	16	55	5.3 to 213

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Table 2. Comparison of concentrations of selected organics in the atmosphere (in nanograms per cubic meter).

Compound	Enewetak	North Atlantic	Gulf of Mexico	College Station, Texas	Pigeon Key, Florida
PCB (Aroclor 1242)	0.54	1.84		< 1	
PCB (Aroclor 1254)	0.06	0.69	0.40		0.41
DDE	0.003	0.006	0.083	0.34	0.04
Di-*n*-butyl phthalate	0.9	1.0	1.3	3.8	18.5
Di(2-ethylhexyl) phthalate	1.4	2.9	1.2	2.4	16.6
Hexachlorobenzene	0.10	0.15		0.20	0.12
α-Hexachlorobenzene	0.25	0.39		> 0.42	
Dieldrin	0.010	(0.02)*		0.07	
Chlordane (γ and α)	0.012	(0.03)*		1.26	

*Bidleman *et al.* (*4*), Bermuda.

studies of PCB's in the marine atmosphere have reported PCB's as the heavier Aroclor 1254 or 1248 (*2-4*), although recent workers in the Great Lakes regions reported a significant amount of the Aroclor 1242 isomers (*7, 14*). The reported differences in atmospheric PCB's may be related to analytical and sampling procedures (*15*), although we believe that our own samples from the different locations (Gulf of Mexico and Enewetak Atoll) are due to real differences resulting from the atmospheric lifetime of different PCB isomers. This belief is supported by the report that rainfall and dry deposition effectively scavenge the heavy PCB isomers (Aroclor 1254) (*16*). Differential removal rates of PCB isomers would help explain the persistence and preferential long-range transport of Aroclor 1242 to remote marine areas.

Two other organochlorine compounds present in significant quantities in the air samples we collected were HCB and HCH. We are not aware of any other quantitative data for these compounds in the marine atmosphere, although both compounds have been reported in marine organisms (*17*). Rice *et al.* (*18*) reported the presence of HCB in the Bermuda atmosphere, but no concentration estimates were made; HCH has been reported in rain in Canada (*19*), Great Britain (*20*), and Hawaii (*8*). The α-isomer of HCH was found to be the major component of HCH in our samples, although its source is uncertain at this time. Air samples taken in College Station, Texas, and in the Sargasso Sea also contain α-HCH and HCB but in concentrations higher than those measured at Enewetak (see Table 2). These data suggest that HCB and HCH are well mixed in the atmosphere and have a widespread distribution in the Northern Hemisphere.

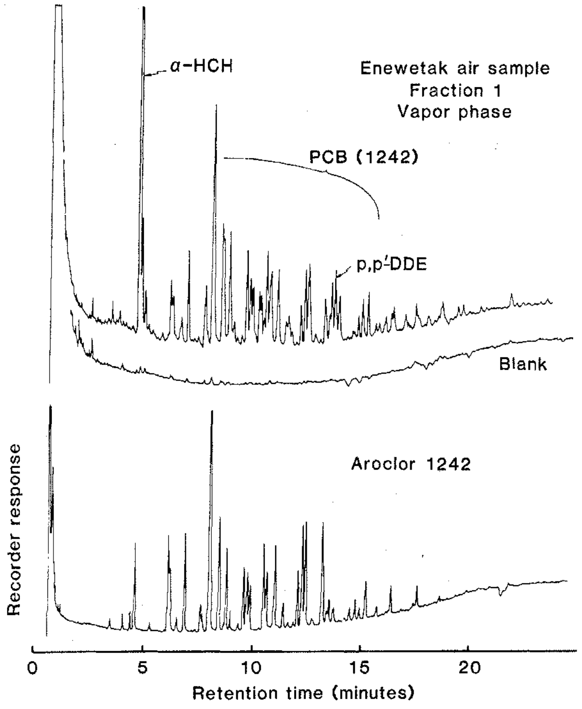

Fig. 1. Electron-capture gas chromatogram of (top) polychlorinated biphenyls (PCB's) and other chlorinated hydrocarbons in an air sample from Enewetak Atoll, (middle) a blank sample, and (bottom) an authentic PCB mixture, Aroclor 1242 (25-m SE-52 WCOT glass capillary column; H_2 carrier, 4 ml/min; 5 percent CH_4 and 95 percent Ar makeup, 25 ml/min; injector temperature, 250°C; detector temperature, 300°C; oven temperature program, 150°C for 5 minutes, 4°C per minute to 210°C, isothermal for 5 minutes).

Analysis of the air samples also revealed small amounts of dieldrin, *cis*- and *trans*-chlordane, lindane (γ-HCH), and *p,p'*-DDE. The concentrations of these compounds are similar to those reported in the North Atlantic (*3, 4*) but are considerably lower than the values in continental regions (Table 2).

Phthalic acid esters were another class of organic pollutant measured in the Enewetak samples. Recently identified as a marine pollutant (*2*), this class of compounds is widely used as a plasticizer additive. Nearly 6×10^8 kg are produced annually in the United States. The concentrations of two plasticizers, di-*n*-butyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), were in the low nanogram-per-cubic-meter range, similar to the concentrations in other marine areas but one to two orders of magnitude lower than reported in urban areas (*21*).

Rain samples had relatively high concentrations of HCH isomers and the phthalate plasticizers; PCB's and the other chlorinated compounds were present at near or below the level of detection. Washout factors for the compounds were calculated from their average rain and atmospheric concentrations. The calculated factors range from < 1 for PCB (Aroclor 1242) to 34 to 38 for the phthalates and γ-HCH. These are similar to the washout factors in nonremote areas reported by Atkins and Eggleton (*22*) and Bidleman and Christensen (*16*). The washout factors for these organic compounds that we measured are lower by a factor of 10 to 1000 than the values for trace metals (*23*). These data indicate that rainout and washout may be relatively inefficient mechanisms for scavenging organic pollutants from the marine atmosphere.

If rain were the only or the primary mechanism for removing organics, unacceptably long residence times would result. Thus, residence times are calculated to be 60 days for phthalates and γ-HCH, 180 days for α-HCH, up to 1 year for *p,p'*-DDE, more than 3 years for chlordane and dieldrin, and up to 6 years for PCB's (Aroclor 1242). However, vapor-phase deposition onto the sea surface should decrease the apparent residence time markedly and may be the controlling factor for the transfer of some organic pollutants to the ocean. If we use PCB (Aroclor 1242) as an example, a vapor deposition velocity of 8 m/hour (*24*) results in a PCB flux from the air to the ocean of approximately 3.5×10^{-5} g m^{-2} year^{-1}. This flux is nearly 60 times the estimated precipitation flux of PCB (Aroclor 1242). A vapor flux of this magnitude would reduce the apparent residence time from 6 years to 30 days. For comparison, we can use Junge's relationship (*25*) between residence time and sample variance to obtain an independent estimate of atmospheric residence time. From our Enewetak data, the residence time of PCB (Aroclor 1242) is calculated to be 189 days. This relatively short residence time further suggests that rainout is not the only removal mechanism for organics in the marine atmosphere.

The data presented here confirm the presence of selected organic pollutants in the atmosphere of remote marine regions and provide a baseline against which future pollutants may be measured. Work is continuing in our laboratory to identify several other unknown compounds in our samples and to estimate the flux of these pollutants across the air-sea interface. In particular, better measurements of the rate of gas exchange of some pollutants are required to obtain an accurate estimate of the transfer of organic pollutants to the ocean. Additional measurements of organic pollutants are also required in the mid- to high-latitude regions if we are to obtain a realistic picture of the distribution of organic pollutants in the marine atmosphere.

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Annual Growth Increments in Shells of *Spisula solidissima* Record Marine Temperature Variability

Abstract. *Systematic variations in annual growth increments, formed over a 16-year period in shells of the marine bivalve mollusc* Spisula solidissima, *reveal more growth in some years than others. Favorable years are indicated by larger than expected annual growth increments and successful recruitment of juveniles. Variations in the size of growth increments correlate negatively with sea surface temperatures. The results suggest that the annual growth increments in the shells of certain molluscs record changes in the marine environment and may be useful monitors of pollution and indicators of paleotemperatures.*

Many species of bivalve molluscs have been reported to contain annual growth increments in their shells (*1*) analogous to tree rings (*2*) or annual growth bands in corals (*3*). Methods borrowed from dendrochronology can be used to assess systematic variations in the size of these increments. Such variations suggest that fluctuations in environmental favorability for growth occurred during certain years. The bivalve shell may thus be considered a recorder of conditions in the marine environment.

I explored the relative value of using annual increments of shell growth in bivalves as environmental indices by examining populations of *Spisula solidissima*, the Atlantic surf clam, collected along the New Jersey coast. For two consecutive years, April 1977 through March 1979, specimens were collected every other week or, during winter, once a month. Examination throughout the year of the growing shell margins of these clams demonstrated the existence of annual increments of shell growth in this species (*4*), confirming the results of an earlier investigation involving marked and recovered clams (*5*). One growth increment, GI-1 (Fig. 1), forms each year in late summer to fall when water temperatures are highest and the animals spawn (*6*). Throughout the remainder of the year, the other growth increment, GI-2 (Fig. 1), is deposited.

Age and growth rate for any surf clam can be determined by measuring successive shell heights of the annual growth increments in a cross section of the shell (*4*-*6*). These measurements provide a relative indication of how much an individual grew in a given year. Caddy and Billard (*7*) have shown that shell growth for inshore surf clams is best described by a von Bertalanffy curve [described in (*7*)] which predicts a slowing of growth rate with size and age. Their study and that of others (*5*) suggest that inshore

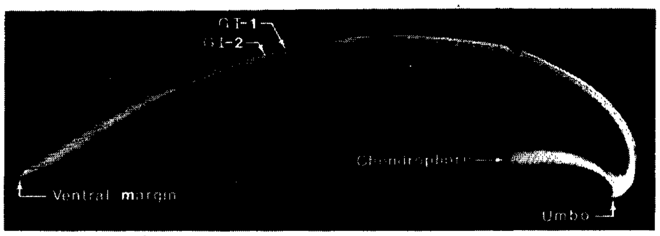

Fig. 1. Radial cross section of surf clam shell. Growth increment GI-1, the thin dark increment, forms annually in the late summer to fall while GI-2, the wider, opaque, white increment, forms during the remainder of the year. The distance between the umbo and the contact of GI-1 with the external shell surface is the shell height for any given year. The difference between successive shell heights is used as the measure of the annual growth increment in shell size. Shell height is 125 mm.