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Hexachlorophene Distributions in Estuarine Sediments

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Hexachlorophene (HCP), or 2,2'-methylenebis(3,4,6-trichlorophenol), is a powerful bacteriostatic agent and germicide that was used widely in the U.S. until 1972. In 1972, the U.S. Food and Drug Administration limited the use of HCP to prescription products and banned the over-the-counter sale of cosmetics and drugs containing more than 0.1 % HCP. HCP has been produced and/or sold in the U.S. through the 1970's and 1980's, although statistics on production/sales are not readily available (U.S. International Trade Commission). There is little documentation of the environmental occurrence of HCP; a literature search revealed only one paper describing HCP distributions in sediments (Sims and Pfaender 1975). Available data suggest that HCP is persistent in the environment. A laboratory study revealed that HCP was apparently not degraded in river water and had a "half-life" of 290 days in estuarine sediments at 22° C (Lee and Ryan 1979).

This paper reports the observed distribution of HCP in sediments collected from two East coast sites during or after 1980 (eight years after the U.S. FDA ban). Data were not collected on spatial distributions of HCP; rather, geochemical data were collected on the distribution of HCP among different organic matter fractions of sediment samples. The detection of HCP was an unexpected result of a study designed to describe the distribution of three classes of organic compounds (PCBs, petroleum hydrocarbons, and fatty acids) among the following three sedimentary organic matter fractions: (1) free lipids, or solvent-extractable organic matter, (2) humic acid, or base-soluble, acid-insoluble organic matter, and (3) humin, or refractory organic matter that is not soluble in solvent, base, or acid. Discussion of results for PCBs, hydrocarbons, and fatty acids are presented in Beller and Simoneit (1986) and Beller (1985).

MATERIALS AND METHODS

Figure 1 presents a flow diagram of the selective extraction procedure used to isolate organic compounds (e.g., HCP) from the free lipid (FL), humic acid (HA), and humin (HU) fractions. The procedure was designed to effect exhaustive extractions at each stage and to treat FL, HA, and HU fractions as similarly as possible. Dried sediment samples (ca. 90 to 140 g, dry weight) were Soxhlet extracted with azeotropic toluene/methanol (1:3, v/v) for over 95 cycles with a solvent change at 30 hr; all solvents (Burdick and Jackson) were distilled in glass and were of high purity. Humic substances were extracted with five successive one-liter additions of solvent-cleaned 0.2N KOH. The

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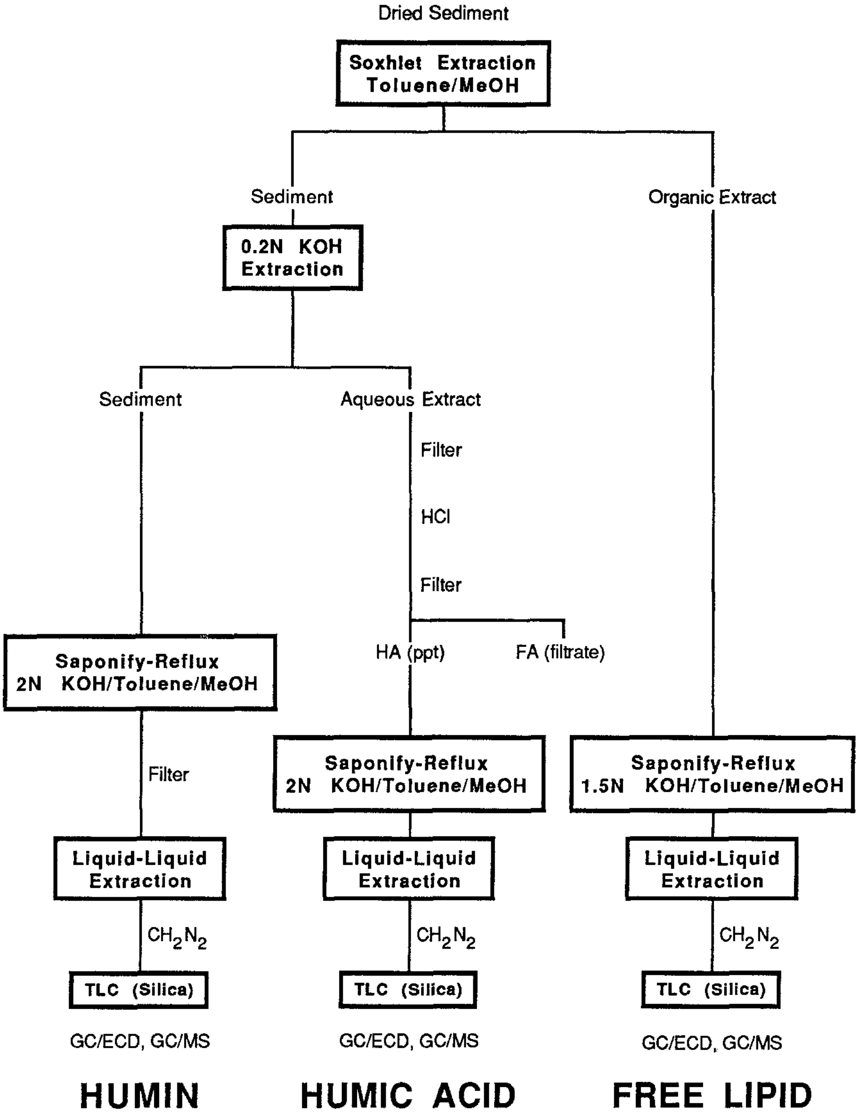

Figure 1. Flow diagram of selective extraction procedure.

combined aqueous extract was filtered through a Whatman GF/A glass fiber filter (to remove suspended particles from the extract), acidified (to precipitate the humic acid), and re-filtered (to separate humic and fulvic acids). The humic acid precipitate was rinsed through the filter with 0.2N KOH, resulting in a basic humic extract without fine particles. The filters and trapped particles were added to the residual sediment. The purpose of saponifying humic fractions was to disperse the polymers in the presence of organic solvents, thus releasing entrapped or sorbed compounds. The KOH may also have hydrolyzed HCP from organic matter and probably acted as a good solvent for HCP that had not already been extracted with toluene/methanol. The FL extracts were saponified to make them comparable to HA and HU extracts. Separatory funnel extractions of saponified extracts were performed at pH >12 and at pH <2. The organic extracts from liquid-liquid extraction were rotary evaporated to near dryness and derivatized with diazomethane (CH_2N_2) according to the procedure of Fales et al. (1973). Derivatized extracts were subjected to preparatory thin layer chromatography (TLC) on Analtech silica GHL plates; the elution solvent was 6.6% diethyl ether in hexane. HCP (derivatized as a dimethyl ether) was unintentionally collected with the TLC band containing aliphatic hydrocarbons and PCBs. These fractions were dissolved in hexane and treated with metallic mercury to remove elemental sulfur before gas chromatographic analysis (GC/ECD and GC/MS). Gas chromatographic conditions are described elsewhere (Beller and Simoneit 1986). The identity of HCP was confirmed by comparison of retention times and mass spectra to those of a methylated standard. Salient features of the mass spectrum of methylated HCP are as follows: m/z 189 (base peak), m/z 191 (74% intensity), m/z 209 (25% intensity; Cl_3 fragment), m/z 223 (54% intensity; Cl_3 fragment), and m/z 434 (19% intensity; parent ion). The unmethylated HCP spectrum is described in Buhler et al. (1973).

The samples with detected HCP are described briefly below. Based on the initial objectives of this study, samples were chosen primarily for their known PCB contamination. Sample NB(0-3) was derived from the 0-3 cm horizon of a large volume box core taken at Station 67 of Summerhayes et al. (1977) in Buzzards Bay, near New Bedford, Massachusetts. The sample was collected in 1983 and was stored frozen. The sedimentation rate at this site, which borders a dredged navigation channel, is unknown. The organic carbon content of NB(0-3) was 5.8%. Sulfides, indicative of sulfate-reducing conditions, were prevalent in this sample.

Sample HR was collected in 1980 with a Shipek grab sampler from a marginal cove in the Hudson River, approximately 60 river miles north of the southern tip of Manhattan (Bopp et al. 1981). The organic carbon content of Sample HR was 3.7%. The sample consisted of the top 10 cm of sediment, which according to a ^{137}Cs profile of this core, encompassed 25 years of sedimentation (Dr. R. Bopp, personal communication).

RESULTS AND DISCUSSION

HCP was detected in samples from the Hudson River (Sample HR) and New Bedford [Sample NB(0-3)] and was not detected in any blanks. HCP distribution among organic matter fractions was identical in both samples: it was detected only in the humic acid fraction, not in the solvent-extractable (FL) or humin fractions. A set of GC/ECD chromatograms representing this distribution in Sample HR is presented in Figure 2. Because the chromatograms are at different attenuations and the extracts were at different dilutions, the relative amount of sediment represented by each fraction is presented in the figure caption. Although a peak in the FL fraction eluted at the retention time of HCP, GC/MS ion chromatograms demonstrated that HCP was not present in the FL extract. Other peaks in the chromatograms are mostly PCB congeners, although pentachlorophenol was also detected in all fractions of these samples. A striking aspect of Figure 2 is that HCP was the predominant compound in the humic acid (HA) extract; few other peaks were apparent.

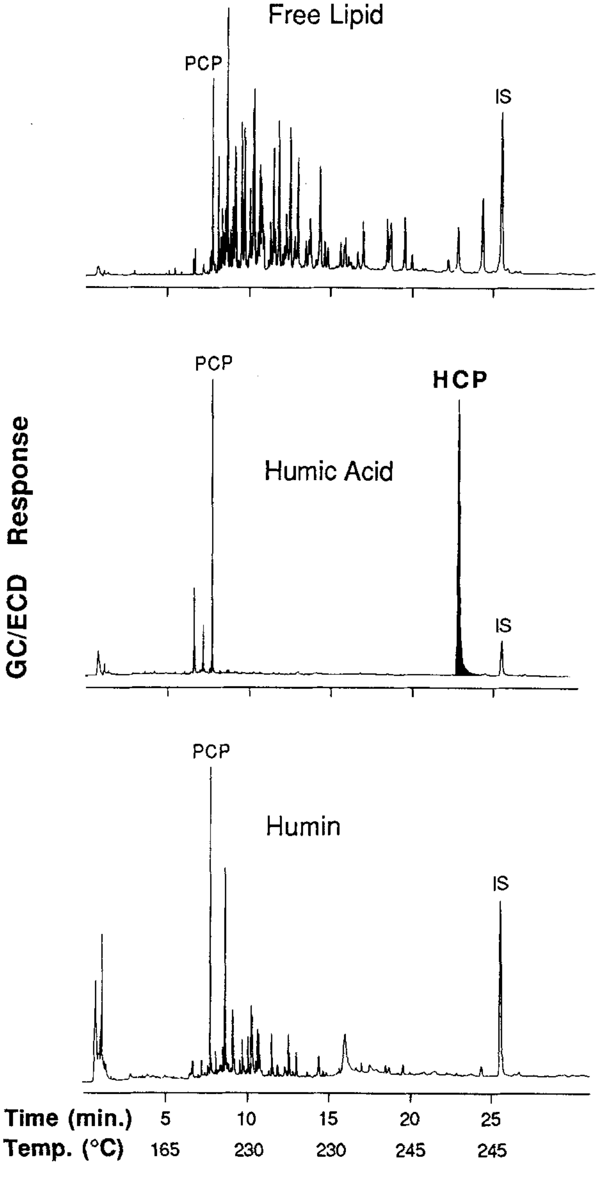

Figure 2. Capillary GC/ECD traces of free lipid (FL), humic acid (HA), and humin (HU) fractions of the Hudson River sediment sample. PCP - pentachlorophenol (methyl ether derivative); HCP - hexachlorophene (dimethyl ether derivative); IS - injection standard, decachlorobiphenyl. Accounting for the different extract dilutions and plot attenuations for the three fractions, the relative amounts of sediment represented by the fractions are roughly 1:12:19 (FL/HA/HU).

HCP was also a predominant peak in the HA extract of the New Bedford sample, although it was not the largest peak.

The occurrence of HCP only in humic acid fractions suggests that the pollutant was strongly associated with organic matter. HCP may have been covalently bound to organic matter and released hydrolytically during treatment with KOH. Laboratory studies support these observations: Miller et al. (1978) demonstrated that HCP covalently binds to rat tissue protein (in vitro) and Mathur and Morley (1978) showed that a structurally similar compound, methoxychlor [2,2'-bis(p-methoxyphenyl)1,1,1-trichloroethane], strongly associated with a synthetic humic acid. Murthy et al. (1979) found that a portion of pentachlorophenol spiked into soils became bound to humic acid and humin fractions after 24 days of laboratory incubation under aerobic and anaerobic conditions.

The following points can be drawn from the observed distribution of HCP in this study:

1) HCP was detected only in humic acid fractions of the two samples in which it was observed; these samples were collected at least eight years after the FDA ban. Thus, HCP can bind strongly to organic matter and appears to be highly resistant to degradation in that form.

2) Conventional solvent extraction techniques may be insufficient to fully characterize sediment contamination by ionizable organic compounds such as HCP. This is particularly relevant to routine U.S. EPA analyses for semivolatile organic compounds in soil/sediment (U.S. EPA 1986), which rely on methylene chloride or methylene chloride/acetone extraction to recover polar compounds such as chlorinated phenols.

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