$\tilde{V}_A$	molar volume of solute (cm^3 mol^{-1})
x	distance (cm)
$\bar{x}$	dimensionless distance
α	dimensionless solution concentration
β	dimensionless adsorbed concentration
Γ	TCDD concentration adsorbed to particle surfaces (g cm^{-2})
Γ_0	initial TCDD concentration adsorbed to particle surfaces (g cm^{-2})
ϵ	porosity (cm^3 cm^{-3})
ϵ_l	fluid-filled porosity (volume wetness) (cm^3 cm^{-3})
ϵ_p	fraction of total volume occupied by particles (cm^3 cm^{-3})
θ	fraction of surface area left open for adsorption
μ	viscosity (cP)
ρ_p	particle density (g cm^3)
τ	tortuosity
Ψ_B	association parameter for use in Wilke–Chang estimation

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Surface Reactions of Brominated Arenes as a Model for the Formation of Chlorinated Dibenzodioxins and -furans in Incineration: Inhibition by Ethanolamine

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■ The aryl coupling reaction of bromobenzene on alumina-supported copper catalysts has been studied as model for dioxin formation. The reaction was monitored in situ by transmittance FTIR spectroscopy. Time-dependent changes in the spectra were recorded during addition of bromobenzene to the carrier gas stream. Both coupling of phenyl intermediates to yield biphenyls and formation of phenol and phenolate were observed. Novel approaches to inhibit the coupling reaction of aryl halides by addition of ethanolamine to the catalyst surface were studied. The resulting inhibition was attributed to site blocking and irreversible deactivation of the copper surface due to imine and nitride formation.

Introduction

The mechanisms leading to the formation of chlorinated dibenzodioxins and -furans (PCDD/F) generated during incineration processes, e.g., in municipal waste incineration (MWI), are a subject of current research interest and controversial discussion (*1, 2*). Evidence is emerging that catalytic reactions occurring between 300 and 400 °C on the surface of fly-ash particles in the postcombustion zone play an important role in the formation of these micropollutants (*3–6*). Fly ash has been identified as a catalytically active reagent for electrophilic chlorination of aromatic structures (*7*). Halogenation and dehalogenation reactions of aryl bromides catalyzed by fly ash from MWI at 300 °C (*8*) have recently been observed.

As a consequence of these findings an inhibition method has been developed (*9*), which is based on deactivation of the catalytic surfaces of fly-ash particles through the addition of suitable compounds (*9*) to the postcombustion zone. The results of appropriate laboratory experiments (*10*) have been extended to a technical pilot plant burning refuse-derived fuel (RDF); an overall reduction of PCDD/F concentration by 96% has been observed (*11*). The results of preliminary experiments in a technical plant have also been reported (*12*).

In order to obtain a more detailed understanding of the heterogeneous chemical reactions occurring on the fly-ash surfaces we have tested an appropriate catalytic model

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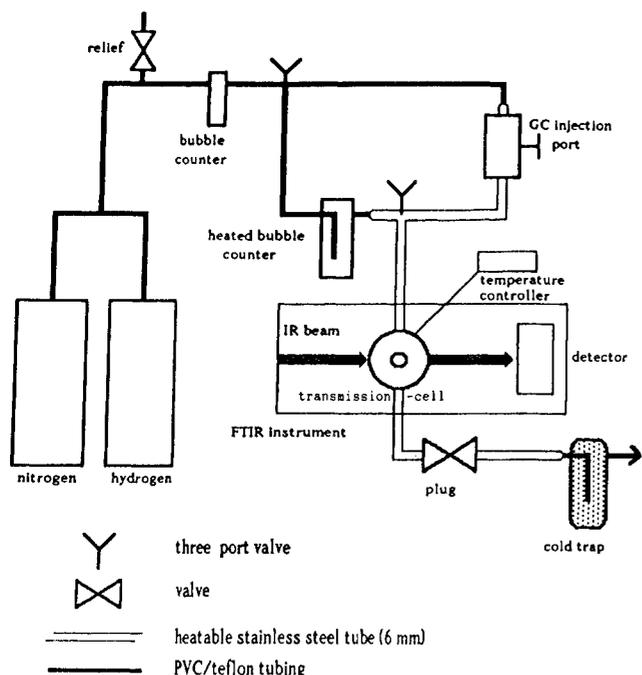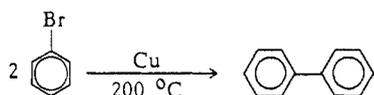
Figure 1. Block diagram of the apparatus used for the in situ transmittance FTIR experiments.

reaction, i.e., the conversion of bromobenzene to biphenyl on a copper surface (Ullmann I reaction).

$$2\ \underset{}{\overset{Br}{\bigcirc}} \xrightarrow[200\ ^{\circ}C]{Cu} \bigcirc\!\!-\!\!\bigcirc$$

Copper-catalyzed coupling reactions of halogenated arenes (Ullmann type I reaction) have been the subject of extensive investigations (13); a strong dependence on the method of preparation of the copper particles has been found (13).

This reaction is widely used for syntheses of various bisaryl compounds in organic chemistry (14), and several mechanistic pathways have been proposed (13, 14). As the effluents of MWI plants contain chlorobenzenes and chlorophenols, this reaction and the corresponding Ullmann type II reaction (15) (formation of bisaryl ether compounds from halobenzenes and phenols) can be used as a model for the formation of halogenated biphenyls, dibenzodioxins, and dibenzofurans. Copper has been detected in MWI fly ash (16) and is considered to act as a catalyst in the formation of PCDD/F. The conversion of chlorophenols to chlorinated dibenzodioxins at ca. 300 °C on the surface of catalytically active fly-ash particles has been demonstrated (9) experimentally.

An analysis system has been developed to study this reaction by surface-sensitive transmittance FTIR spectroscopy (17). The effect and fate of two established inhibitors, triethylamine and ethanolamine, were studied in detail by use of this method. Reference information used for the spectral interpretation includes the work of Kagel (18), who studied the adsorption of 1-(o-chlorophenyl)-ethanol, as well as recent spectroscopic investigation on copper catalysts (19–21). A more extensive survey on spectroscopic references is given in ref 17.

Experimental Section

Apparatus. An in situ transmission cell similar to the one used by Hecker and Bell (22) was used for the FTIR investigations. A block diagram of the apparatus is presented in Figure 1. The temperature in the reactor
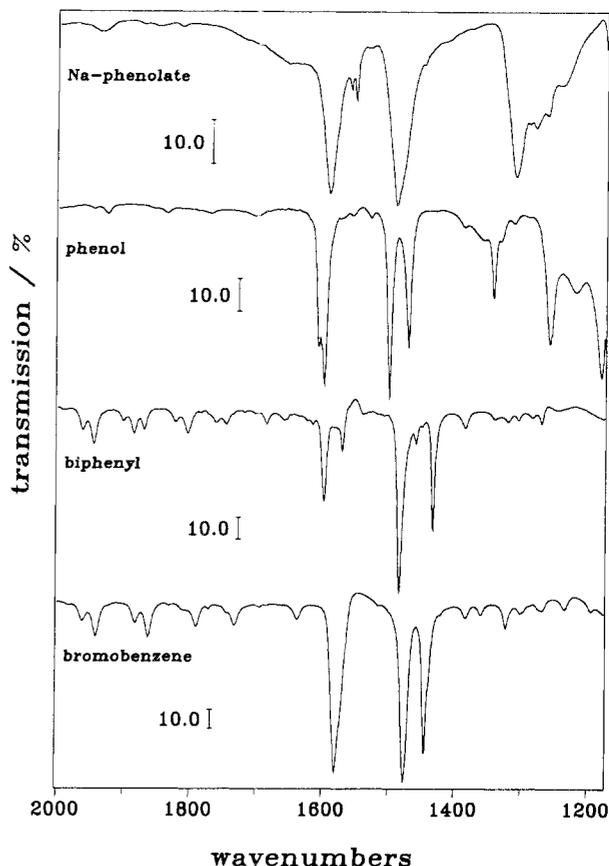
Figure 2. FTIR spectra of reference compounds recorded at room temperature in transmission.

was controlled to within ±3 K. Stepwise addition of the reactant was achieved by redirecting the carrier gas stream through a heated bubble column containing the reactant; the concentration was adjusted by varying the temperature of the bubble column. Alternatively, reactants were added in a pulsewise fashion through a modified gas chromatography injection port. The system is a slightly modified version of a design described in ref 19. Spectra were recorded with an FTIR instrument (Mattson, Model Polaris) equipped with a transmission cell; 25 scans at a resolution of 4 cm^{-1} were coadded for each spectrum at a given temperature.

Subsequent to the spectroscopic experiments, the contents of the cold trap as well as compounds adsorbed on the catalyst material were analyzed by GC/MS (Hewlett-Packard, gas chromatograph, Model 5890 A, and mass selective detector, Model 5970).

Reagents. Traces of water were removed from bromobenzene (Aldrich, purity >98%) by storing the liquid over a molecular sieve. Ethanolamine (Aldrich, >98%) and triethylamine (Fluka, p.a.) were used without purification.

Catalysts: Preparation and Pretreatment. The catalyst, which contained 10 wt % of copper on alumina, was prepared according to the procedure described elsewhere (23). The alumina modification of the support was identified as γ-Al$_2$O$_3$ by X-ray diffraction. For the IR studies, 40 mg of the catalyst was pressed into thin wafers of 20-mm diameter, using a pressure of 12 tons cm^{-2}. The catalyst wafers were pretreated in a flow (35 cm^3 min^{-1}) of pure nitrogen (Linde, 99.999%) at 473 K for 2 h.

Results and Discussion

1. Reactions of Bromobenzene on Copper Catalyst Surfaces. Reference spectra of sodium phenolate, phenol, biphenyl, and bromobenzene recorded at room tempera-
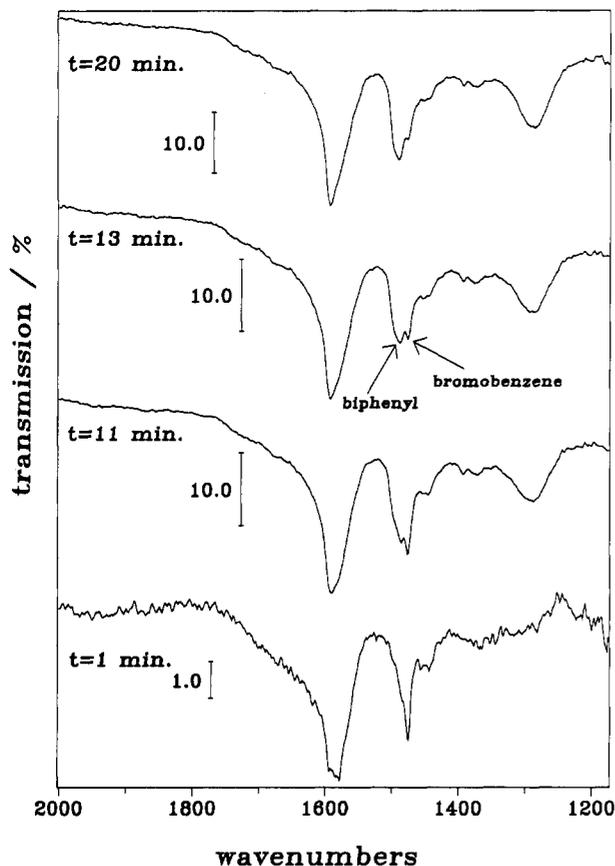
Figure 3. Time-dependent transmittance FTIR spectra recorded over a Cu/γ-Al₂O₃ catalyst surface at 200 °C, subsequent to stepwise addition of bromobenzene to the nitrogen carrier gas stream. Experimental conditions are described in the text.

ture in the setup described above are presented in Figure 2. The reactions of bromobenzene on the surface of our copper/γ-Al₂O₃ catalyst at 200 °C were followed over a period of 20 min (Figure 3).

The reaction of bromobenzene, to yield biphenyl, is clearly seen from the appearance of the corresponding biphenyl absorptions in the FTIR spectra. In particular, one observes the time-dependent growth of the characteristic 1483-cm⁻¹ vibration of biphenyl on the high-frequency side of the 1474-cm⁻¹ band of bromobenzene (cf. spectrum recorded at t = 13 min in Figure 3). In ref 17, various types of catalyst surfaces have been compared with respect to the observed rate of biphenyl formation. Copper/γ-Al₂O₃ catalysts are generally more active than Cu/gibbsite systems. The activity of Cu/γ-Al₂O₃ is increased by in situ reduction of the copper, followed by dehydration. Tables summarizing the relative dehalogenation activities, as well as details of the spectroscopic assignments for reactant and product bands, are given in ref 17.

Note that the 1445-cm⁻¹ vibration of biphenyl, and the corresponding 1432-cm⁻¹ feature of bromobenzene, are comparatively weak on the catalyst surface. These vibrations are characterized by a dynamic dipole moment that is parallel to the surface and is therefore screened by the presence of metallic copper. A mechanism for biphenyl formation that involves copper organic species on the surface of the catalyst is proposed in the reaction scheme of Figure 4. In addition, formation of phenolate is observed. This side reaction is generally not observed when the reaction is performed in solution (13, 14). The reaction conditions on the solid phase may favor a substitution reaction of the aryl bromide with nucleophilic O²⁻ anions
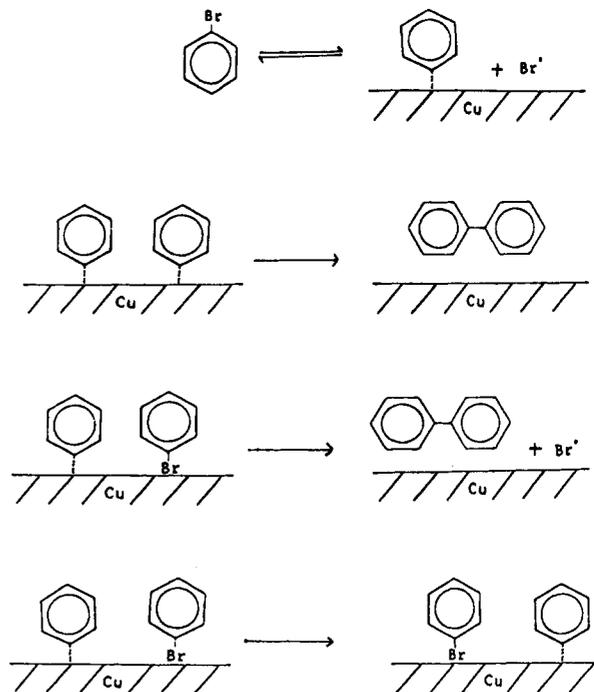

Figure 4. Proposed mechanism for reactions of bromobenzene over a copper catalyst surface. Subsequent to adsorption and formation of a surface phenyl species (top), biphenyl is formed by a recombination reaction (second trace) or reaction of a surface phenyl species with the bromobenzene reactant (third trace). In addition, halide-exchange reactions are known to occur on the copper surface (bottom trace).

of the support material (γ-Al₂O₃).

The presence of the biphenyl product was verified by GC/MS analysis of the contents of the cold trap subsequent to the spectroscopic runs. Furthermore, biphenyl was identified upon extraction of the spent catalyst with CCl₄, followed by GC/MS analysis.

2. Effects of Inhibitors. The reaction of chlorophenols to chlorinated dibenzodioxins occurring on the surface of various fly-ash samples from standard MWI reactions has been used as model for PCDD/F formation (9, 10).

$$2 \overset{OH}{\underset{}{\bigcirc}}-Cl_x \xrightarrow[300\ ^\circ C]{\text{fly-ash}} Cl_y-\bigcirc\overset{O}{\underset{O}{\bigcirc}}-Cl_z$$
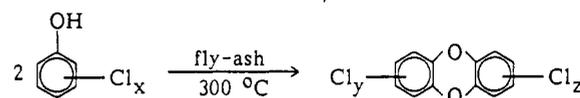
A set of 11 compounds was tested for their ability to block the reaction (9, 10). Alkanolamines, such as triethanolamine and ethanolamine, were found to be most efficient as inhibitors. The dose–response relationship has been studied for the triethanolamine inhibitor (9).

Encouraged by this success, the laboratory experiments have been transferred to a pilot plant incinerator burning a special kind of refuse-derived fuel. By an appropriate technique, a mixture of triethanolamine and triethylamine was added to the stack gas in the 400 °C postcombustion zone. The addition (1:1) resulted in a significant overall reduction of the PCDD/F concentration, by a factor of 12–15 (9). It is worthwhile mentioning that the incinerator must be operated with inhibitor injection for an induction period of about 12 h before the full reduction in PCDD/F levels is achieved (8, 9). Some preliminary results of inhibition studies on a larger technical municipal waste incinerator have also been reported (12, 24).

To understand the mechanism of inhibition, ethanolamine was added together with bromobenzene to the copper catalyst described above, and the surface reactions were studied at 200 °C. Ethanolamine was added pulsewise into a continuous stream of bromobenzene passing
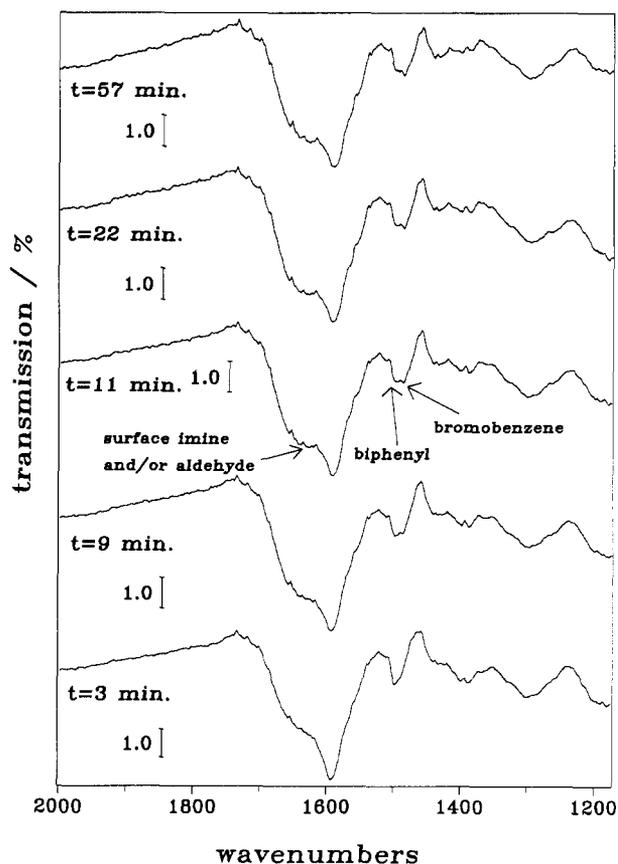
Figure 5. Time dependence of transmittance FTIR spectra recorded over a Cu/γ-Al$_2$O$_3$ catalyst at 200 °C, subsequent to ethanolamine addition to a continuous bromobenzene/nitrogen carrier gas stream. Note that the biphenyl product, which initially prevails on the surface, is progressively displaced by the bromobenzene reactant as the catalyst is being deactivated by ethanolamine. Additional surface species observed are discussed in the text.

Figure 6. Surface species produced by addition of the ethanolamine inhibitor to the copper catalyst surface. The series of time-dependent spectra shown in Figure 5 is extended to longer reaction times. Attention is focused on the 2100–2300-cm^{-1} region, where vibrations of surface azides and cyanides are being observed (see text).

over the surface, while the reaction was monitored by FTIR; see Figure 5.

The addition of ethanolamine to the reaction system by this technique was observed to block the formation of biphenyl from bromobenzene. In the presence of ethanolamine, bromobenzene resides on the catalyst surface without further reaction to products. In a complementary experiment, it was impossible to detect a 5-μL pulse of bromobenzene on a catalyst surface loaded with ethanolamine before addition of bromobenzene. The control experiment, performed in the absence of ethanolamine, proved that 5 μL of bromobenzene is easily detected on the catalyst surface over a period of 90 min. The reaction and fate of the inhibitor, ethanolamine, can be deduced from new bands observed between 2100 and 2300 cm^{-1}, and a broad band extending from 1610 to 1680 cm^{-1} which is assigned to a surface-bound aldehyde (19) or a surface imine species (21, 25). The bands in the 2100–2300-cm^{-1} range are attributed to either azide or cyanide groups formed on the surface of the catalyst (cf. Figure 6). The width and intensity of these bands correspond to those observed in the spectra reported in refs 20 and 21. Azides and imines have been found as intermediates during reaction of primary alkylamines on transition-metal surfaces, in which nitrides are formed as the final state of deactivation (21, 26, 27). It is known that these surface species deactivate the copper catalyst surfaces in various catalytic reactions, such as the dehydroamination reaction (26).

The model of catalyst deactivation by nitride formation is supported by the fact that nitrogen, as well as bromine, is detected in an energy-dispersive X-ray analysis of the catalyst surface subsequent to the inhibition run.
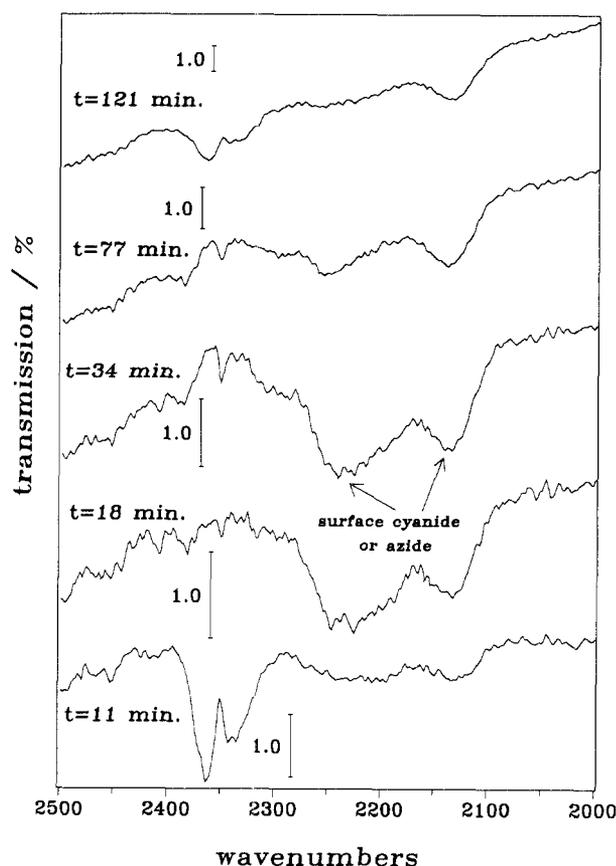
In an experiment using triethylamine, no evidence for a corresponding inhibitory action was found. We only observed a band at 1653 cm^{-1}, which is due to a surface imine (25). This is consistent with the laboratory inhibition tests (11).

In summary, it appears that amines are well suited to inhibit the catalytic action of copper. Primary amines are converted to copper nitride, and the catalyst is deactivated by the formation of the nitride layers. Tertiary amines, such as triethylamine, for which nitride formation has not been observed, are less active as inhibitors.

The second mechanism of inhibition identified in this study is the displacement of the aryl dehalogenation by competitive reactions that are favored on the catalyst surface by preferential adsorption. The dehydroamination reaction, which is known to inhibit other catalytic processes on copper surfaces (26), has been identified as a likely candidate for the competitive inhibition mechanism. The inhibitor studied, ethanolamine, contains both the amine and the alcohol functionalities required for this reaction. The γ-alumina support provides strong adsorption sites for the hydroxyl group of the inhibitor. During dehydroamination, an aldehyde intermediate is formed; the observation of this species provides evidence for the involvement of this reaction in the inhibitory action of ethanolamine.

Conclusion

The conversion of bromobenzene to biphenyl on a defined copper catalyst surface has been monitored by FTIR spectroscopy. By use of this reaction as a model for

PCDD/F formation on fly ashes, the effect of inhibitors was studied by this technique. While no inhibitory action was observed for triethylamine, ethanolamine was shown to act as a very efficient inhibitor, by blocking the active sites of copper surfaces. At this point it is important to draw attention to the differences between the carefully prepared surfaces investigated in this study, and the highly heterogeneous fly ash in the complex environment of an incinerator. Details of the phenomena observed in the laboratory cannot be transferred to the technical plant, and we cannot exclude the possiblity that other modes of inhibitory action are important in the incinerator environment. However, the relevant results on the inhibition of dioxin formation obtained in the pilot plant are consistent with the mechanisms proposed in this study.

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Role of Plant Biomass in the Global Environmental Partitioning of Chlorinated Hydrocarbons

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■ Plant biomass plays a significant role in the global environmental partitioning phenomena and plants are good indicators of tropospheric contamination levels by chlorinated hydrocarbons. In the present research 300 samples of plants were collected in 26 areas distributed worldwide and analyzed for HCB, α-HCH, γ-HCH, *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE. Global HCB distribution is strongly dependent on the temperature, the HCB being present mainly in samples from cold areas. The sum of DDTs show higher concentrations in samples from tropical areas, while the sum of HCHs is higher in the plants from the Northern Hemisphere. These results are discussed, taking into account the role of physicochemical properties in determining the global distribution as well as the air concentrations, the use patterns of the chemicals, and the age of the contamination.

Introduction

In recent years there has been increasing interest in global contamination from persistent organic chemical substances, such as chlorinated hydrocarbons. Concentrations in air have been measured and attempts have been made to evaluate the role of the atmosphere in world transport and contamination of remote areas (*1–3*).

Some groups have attempted to reconstruct the cycling mechanisms of these molecules (*4*), others to quantify the atmospheric inputs to the world's oceans (*5*) and to compile a global mass balance (*6*).

Remote and especially cold areas have been the subject of particular attention and analyses of atmospheric chlorinated pesticides have been performed in Antarctica, Sweden, and Arctic Canada (*2, 7, 8*).

In terrestrial ecosystems, plant biomass is believed to play a significant role in the circulation and bioaccumulation phenomena of these chemicals, and the air to leaf transfer of gaseous organics can be considered a key process, particularly for less soluble compounds (*9–14*).

To contribute to a better understanding of both issues, this research group has measured chlorinated hydrocarbons in foliage as an indication of tropospheric contamination levels (*15*), their contents in lichen and moss samples from the Antarctic Peninsula as base-line levels of world contamination (*16*), and organochlorine residues in mango foliage from West Africa (*17*). This paper is an

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