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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 possibility 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.

Acknowledgments

We thank O. Hutzinger for his support, and M. McLachlan for reading the manuscript.

Registry No. Cu, 7440-50-8; PhOH, 108-95-2; Ph₂, 92-52-4; BrPh, 108-86-1; sodium phenolate, 139-02-6; ethanolamine, 141-43-5.

Literature Cited

- (1) Altwicker, E. R.; Schonberg, J. S.; Konduri, R. K. N. V.; Milligan, M. S. *Chemosphere* 1990, 20, 1935.
- (2) Shaub, W. M.; Tsang, W. *Environ. Sci. Technol.* 1983, 17, 721.
- (3) Karasek, F. W.; Dickson, L. C. *Science* 1987, 237, 754.
- (4) Vogg, H.; Stieglitz, L. *Chemosphere* 1986, 15, 1373.
- (5) Hagenmaier, H. P.; Kraft, M.; Brunner, H.; Haag, R. *Environ. Sci. Technol.* 1987, 21, 1080.
- (6) Gullett, B. K.; Bruce, K. R.; Beach, L. O. *Chemosphere* 1990, 21, 1945.

- (7) Hoffmann, R. V.; Eicemann, G. A.; Long, Y.-T.; Collins, M. C.; Lu, M.-Q. *Environ. Sci. Technol.* 1990, 24, 1635.
- (8) Zier, B.; Lenoir, D.; Lahaniatis, E.; Kettrup, A. *Chemosphere*, in press.
- (9) Dickson, L. C.; Lenoir, D.; Hutzinger, O.; Naikwadi, K. P.; Karasek, F. W. *Chemosphere* 1989, 19, 1435.
- (10) Lenoir, L.; Dickson, L. C.; Hutzinger, O. *Chemosphere*, in press.
- (11) Lenoir, D.; Hutzinger, O.; Mützenich, E.; Horsch, K. Z. *UWSF Umweltchem. Okotox.* 1990, 1, 3.
- (12) Karasek, F.; Naikwadi, K. P. *Proceedings of "Dioxin 90"*; Ecoinforma: Bayreuth, Germany, 1990; Vol. 3, p 127.
- (13) Fanta, P. E. *Synthesis* 1974, 1, 9.
- (14) Koshelev, V. J. *Ser. Khim. Nauk.* 1983, No. 4, 86.
- (15) Moroz, A. A.; Shvartsberg, M. S. *Russ. Chem. Rev. (Engl. Transl.)* 1974, 43, 1443.
- (16) Dickson, L. C. Thesis, Waterloo, 1987; p 112.
- (17) Lippert, T.; Lenoir, D.; Wokaun, A. *Ber. Bunsenges. Phys. Chem.* 1990, 94, 1465.
- (18) Kagel, R. O. *J. Catal.* 1970, 16, 316.
- (19) Jobson, J.; Baiker, A.; Wokaun, A. *Ber. Bunsenges. Phys. Chem.* 1989, 93, 64.
- (20) Jobson, E.; Baiker, A.; Wokaun, A. *J. Chem. Soc., Faraday Trans.* 1990, 86, 1131.
- (21) Kritzenberger, J.; Jobson, J.; Wokaun, A.; Baiker, A. *Catal. Lett.* 1990, 5, 73.
- (22) Hecker, W. C.; Bell, A. T. *J. Catal.* 1981, 71, 216.
- (23) Baiker, A.; Richarz, W. *Synth. Commun.* 1987, 8, 27.
- (24) Morello, T.; Eng, P. *Proceedings, Meeting on Dioxin Inhibition in MWI Plants*, Augsburg, April 2, 1990.
- (25) Sokoll, R.; Hobert, H.; Schmuck, J. *J. Catal.* 1990, 121, 153.
- (26) Baiker, A.; Kijenski, J. *Catal. Rev. Sci. Eng.* 1985, 27, 653.
- (27) Baiker, A.; Monti, D.; Son Fan, Y. *J. Catal.* 1984, 88, 81.

Received for review December 1, 1990. Revised manuscript received April 29, 1991. Accepted May 3, 1991. This work has been supported by grants of the Deutsche Forschungsgemeinschaft (SFB 213).

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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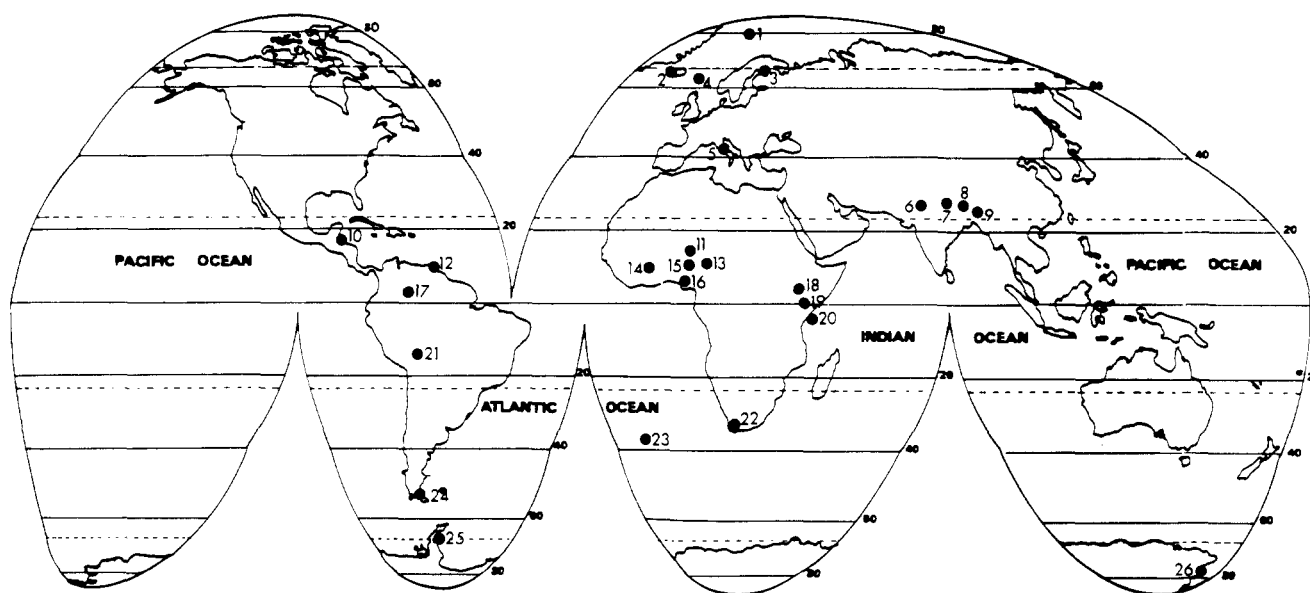


Figure 1. Geographical distribution of the 26 sample sites.

Table I. Information on the 26 Sample Sites

site	lat.	long.	altitude, m	no. of samples	plant species
1. Spitsbergen	78° N	15° E	0	20	lichens, mosses
2. Iceland	65° N	20° W	100-500	8	lichens, mosses
3. Scandinavia	70-60° N	18-33° E	500-700	18	lichens, mosses
4. Foroyar	62° N	7° W	100-500	9	lichens, mosses
5. Italy	46-41° N	9-16° W	100-300	2	lichens
6. New Delhi	29° N	77° E	250	8	mango
7. Nepal	29-27° N	84-87°	800-2500	21	lichens, mosses
8. Nepal Mountains	29-27° N	84-87° E	2500-4700	32	lichens, mosses
9. Everest	28° N	87° E	5600	6	lichens, mosses
10. Guatemala	16-14° N	89-91° W	600-2500	4	mango, lichens
11. Mali-Guinea	12-9° N	8-10° W	200-500	12	mango
12. Delta Amacuro	11-8° N	60-63°	0	7	lichens, mosses
13. Benin Burkina Faso	12-6° N	2° E	0-300	7	mango
14. Ghana Suhum	8° N	1° E	100-200	20	mango
15. Ivory Coast	7° N	5° E	200-500	5	mango
16. Ghana Accra	6° N	1° E	0	32	mango
17. Amazonas	5-4° N	67-68° W	200-500	16	lichens, mosses
18. Mount Kenya	0°	37° E	3100-4900	23	lichens, mosses
19. Kenya Nairobi	1° S	37° E	1700	2	mango
20. Kenya Mombasa	4° S	39° E	0	5	mango
21. Bolivia	18° S	68° W	3800-5300	9	lichens, mosses
22. Capetown	33° S	18° E	0	1	mango
23. Tristan da Cunha	38° S	12° W	0	10	lichens, mosses
24. Tierra del Fuego	54° S	68° W	0	6	lichens, mosses
25. Antarctic Peninsula	65-68° S	65° W	0	12	lichens, mosses
26. Kay Island	74° S	165° E	0	11	lichens, mosses

extension of a previous investigation, analyzing more samples from different areas of the world with the aim of contributing to the understanding and quantification of the global cycling of these xenobiotics.

Materials and Methods

Selection of Foliage Samples. In cold and temperate areas and at high altitudes (above 2500 m), lichen and moss samples were collected. In tropical areas, fallen mango leaves (*Mangifera indica*) were chosen due to their wide distribution.

All the samples were wrapped in aluminum foil, kept cold (~5 °C) whenever possible, and then stored at -20 °C until pretreatment.

Sample Collection. A total of 300 samples (~10 g each) were collected in 26 areas of the world.

A detailed description of the type of sampling would be lengthy and unnecessary but as a general rule in each area

a variable number of samples were collected along transects of tens to hundreds of kilometers of length, which were considered as representative of the entire geographic area.

The sample collectors were, in a few cases, volunteers, but most of the work was done by the authors of this paper within 1985-1988. Two sampling programs in West Africa and in Antarctica were considered necessary for interpreting the results.

Only a few samples were obtained from Iceland, Cape-town, Nairobi, Kenya, and Italy and these were pooled due to the low weight of the biomass but were included in the paper as representative of the areas. Figure 1 shows the sample sites on a world map while Table I gives geographic areas, numbers of samples, types of plants collected, approximate altitudes above sea level, latitude, and longitude.

Chemical Analysis. After partial oven-drying, minced samples were extracted in a Soxhlet apparatus with *n*-hexane as solvent. Residual water content was measured

Table II. Selected Physicochemical Properties of the Molecules Studied

	MW	VP P_{a}^a Pa	water sol C_{s}^a mol/m ³	log K_{ow}	H , Pa m ³ /mol
HCB	284.8	1.5×10^{-3}	1.7×10^{-5}	6.0	88
α -HCH	290.9	3.0×10^{-3}	6.9×10^{-3}	3.8	0.43
γ -HCH	290.9	4.0×10^{-3}	2.4×10^{-2}	3.8	0.17
<i>p,p'</i> -DDT	354.5	2.5×10^{-5}	8.5×10^{-6}	6.0	2.9
<i>o,p'</i> -DDT	354.5	4.5×10^{-4}	8.5×10^{-6}	6.0	53
<i>p,p'</i> -DDE	318.0	8.0×10^{-4}	1.3×10^{-4}	5.0	6.2

^a At 20 °C.

on homogeneous subsamples (105 °C, 24 h). Sulfuric acid cleanup was followed by Florisil column chromatography. Samples were analyzed with a Perkin-Elmer Sigma-3B chromatograph, using a 30 m \times 0.2 mm (i.d.) SPB-5 bonded-phase (0.25- μ m film thickness) fused-silica capillary column from Supelco. Carrier gas: argon-methane 95/5%, 100 kPa, split ratio 66/1; injector and EC detector temperatures were 220 and 280 °C, respectively; oven temperature 100 °C for 10 min to 280 °C at 3 °C/min and maintained for 40 min.

Statistical Treatment of the Data. A log-probit analysis was performed on the foliage concentration of samples from the same area according to a BASIC computer program suggested by Trevors (18) but slightly modified. This statistical approach was used by Bacci et al. (17) and recently has been suggested as appropriate by Travis and Land (19) and by Helsel (20).

A median C50 was calculated for each group of samples. The values corresponding to probit 4 and 6 (C16–C84), indicating the range around the median where ~68% of the results were expected, were also calculated; from these values the slope of the sample distribution line was obtained. A χ^2 test gave an indication of the homogeneity of the sample population and was significant in almost all cases.

Physicochemical Parameters. A review of the literature was performed in order to estimate the main parameters relevant to understanding environmental distribution processes. Table II shows data on vapor pressure, water solubility, and octanol–water partition coefficients (log K_{ow}) critically selected from a number of literature sources (5,21–27).

Vapor pressure data are in good agreement with a series of experimental values recently produced by B. Rordorf (personal communication).

Results

Mean concentrations, calculated as C50, of the six molecules, for the 26 sample sites, are reported in Table III. The χ^2 values and the slopes of the sample distribution lines are also shown in the table.

For hexachlorobenzene (HCB) and for the sum of hexachlorocyclohexanes (HCHs) and DDTs a log-probit analysis has also been performed on the mean values for the different sites in order to obtain a more easily comparable picture of the global range of values.

The distribution lines, reported in Figure 2, indicate that HCB shows relatively low concentrations, with a C50 of 0.12 ng/g. The C50 values for total HCHs and DDTs are more than 1 order of magnitude higher.

The concentrations in plant foliage here reported are consistent with the published data; see, for example, pine needles from several samples in Germany (28), Italy (15), and other European countries (11), lichens from Sweden,

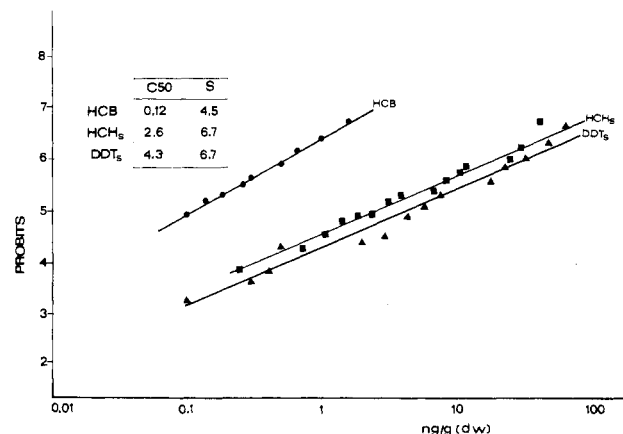


Figure 2. Log-probit distribution of the mean values of concentration in foliage in the 26 sample sites for HCB and the sum of HCHs and DDTs. The C50 values and the slopes (S) are also reported.

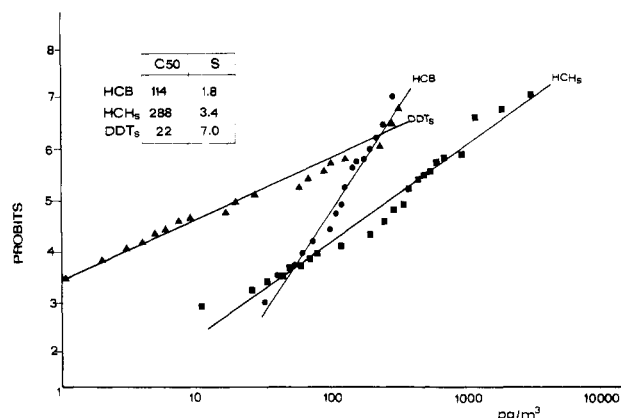


Figure 3. Log-probit distribution of air concentration values for HCB and the sum of HCHs and DDTs taken from the literature (2, 5, 7, 33–35). C50 values and the slopes (S) are also reported.

Norway, and France (29–31), and mango foliage from Colombia (32).

Discussion

Chlorinated hydrocarbons have been found in foliage in all parts of the world. The concentration means and ranges are variable according to the areas studied, but high enough to permit reliable analysis and thus the use of foliage as a biomonitor of presence of chlorinated hydrocarbons even in remote areas where problems may arise for air sampling. Conceptually, this kind of approach could be used to monitor other persistent chemicals with comparable circulation patterns.

As foliage contamination from organochlorinated hydrocarbons is believed to depend on the concentration in the atmosphere (11, 15), a survey of the literature has been made in order to compare global air concentrations with global plant concentrations measured in this work. Figure 3 shows the levels in the atmosphere taken from the literature (2, 5, 7, 33–35) treated with the same log-probit statistical analysis. Results indicate a different ranking among the compounds in comparison with foliage. In air the lowest mean values are for DDTs, in the middle in HCB, and the highest values are for HCHs.

From the global levels in foliage and in air, a bioconcentration factor (BCF) can be calculated as the ratio between the C50 in the two compartments. The values obtained are in good agreement with those experimentally measured in simulation chambers by Bacci et al. (12), as shown in Table IV. This seems to confirm that some

Table III. Mean Concentrations (C50 in ng/g Dry Weight) and Statistical Parameters (χ^2 , Degrees of Freedom (DF), and Slope (S) of the Log-Probit Line for the Organochlorines in the 26 Sample Sites^a

site	HCB	α -HCH	γ -HCH	p,p' -DDT	o,p' -DDT	p,p' -DDE	site	HCB	α -HCH	γ -HCH	p,p' -DDT	o,p' -DDT	p,p' -DDE
1. Spitsbergen							14. Ghana Suhum						
C50	1.00	3.42	0.52	0.30	ND	0.20	C50	<0.1	0.30	2.80	2.40	0.80	0.40
χ^2	4.98	9.44	14.54	7.82		16.40	χ^2	12.60	8.60	2.50	3.50	11.10	
DF	17	17	17	14		14	DF	17	17	17	17	17	
S	2.7	2.2	1.8	1.6		1.7	S	1.7	2.7	2.1	2.0	1.9	
2. Iceland							15. Ivory Coast						
\bar{x}	1.47	4.90	0.78	0.39	ND	0.10	C50	<0.1	0.69	0.35	3.30	0.70	1.60
3. Scandinavia							χ^2	0.38	0.49	0.82	0.82	1.19	
C50	0.68	8.59	3.69	1.60	0.90	0.40	DF	2	2	2	2	2	
χ^2	4.36	3.82	2.05	3.60	8.61	7.18	S	1.6	1.9	1.8	1.4	4.9	
DF	15	15	15	14	14	14	16. Ghana Accra						
S	2.6	2.8	2.7	3.0	3.0	3.3	C50	<0.1	0.30	1.00	15.00	1.50	1.90
4. Föroyar							χ^2	23.60	26.50	44.00	26.10	19.70	
C50	0.27	0.81	0.66	2.90	ND	0.70	DF	29	29	29	29	29	
χ^2	0.42	5.29	0.50	2.45	2.47		S	1.6	1.7	2.9	3.1	2.3	
DF	6	6	6	6		6	17. Amazonas						
S	1.6	2.3	2.0	2.5		4.0	C50	<0.1	41.39	0.15	52.20	7.70	6.50
5. Italy							χ^2	2.11	6.27	3.20	2.98	5.81	
\bar{x}	1.41	26.93	9.95	12.40	ND	8.40	DF	13	13	13	13	13	
6. New Delhi							S	5.3	6.1	10.3	7.8	10.6	
C50	<0.1	106.9	13.55	77.80	10.80	21.00	18. Mount Kenya						
χ^2		0.19	0.60	1.10	0.90	1.70	C50	0.52	7.93	0.78	4.00	1.00	1.10
DF		5	5	5	5	5	χ^2	7.40	4.54	9.75	18.40	8.50	8.10
S		2.4	3.3	1.7	1.4	1.9	DF	20	20	20	20	20	
7. Nepal							S	2.0	2.4	4.4	2.7	4.6	2.1
C50	0.10	21.52	3.46	13.70	2.40	1.90	19. Nairobi, Kenya						
χ^2	4.10	28.42	9.29	15.46	9.20	7.15	\bar{x}	<0.1	1.45	0.88	13.50	2.10	6.70
DF	13	18	18	18	18	18	20. Mombasa, Kenya						
S	2.4	3.1	3.5	3.1	3.0	2.4	C50	<0.1	2.71	0.78	13.80	5.70	25.44
8. Nepal Mountains							χ^2	0.75	0.44	1.06	1.45	0.48	
C50	0.25	35.74	4.47	10.50	4.00	1.60	DF	2	2	2	2	2	
χ^2	6.09	19.42	9.68	3.61	5.15	11.87	S	2.4	1.3	2.0	1.6	1.7	
DF	24	28	28	28	29	28	21. Bolivia						
S	2.6	2.7	2.3	2.4	2.0	2.2	C50	0.18	1.10	0.79	1.20	0.40	0.40
9. Everest							χ^2	1.16	1.23	1.31	0.97	1.28	1.05
C50	0.48	9.50	1.15	2.10	1.80	0.30	DF	6	6	6	6	6	
χ^2	0.63	0.69	0.34	0.75	1.59	1.17	S	1.7	1.9	2.1	2.9	3.6	1.8
DF	3	3	3	3	3	3	22. Capetown						
S	1.8	1.7	1.8	2.4	2.0	2.5	\bar{x}	0.12	0.58	0.77	4.40	<0.1	0.60
10. Guatemala							23. Tristan Da Cunha						
C50	0.14	0.45	0.32	2.90	0.40	1.10	C50	<0.1	0.19	<0.1	ND	ND	ND
χ^2	0.28	0.34	0.55	0.54	0.01	0.10	χ^2	1.39					
DF	4	4	4	4	4	4	DF	7					
S	1.4	1.6	2.2	2.4	3.5	2.8	S	1.5					
11. Mali-Guinea							24. Tierra del Fuego						
C50	<0.1	0.50	0.20	37.00	4.30	8.10	C50	0.15	0.21	<0.1	0.15	0.20	<0.1
χ^2		6.89	5.12	2.25	2.44	1.42	χ^2	0.64	0.68		0.51	1.69	
DF		9	9	9	9	9	DF	3	3		2	2	
S		2.2	2.2	6.2	8.2	4.8	S	1.5	2.7		2.0	1.9	
12. Delta Amacuro							25. Antarctic Peninsula						
C50	<0.1	7.58	0.30	27.50	2.10	2.60	C50	0.49	0.32	0.71	0.30	ND	0.20
χ^2		1.43	1.68	0.45	1.58	1.15	χ^2	2.23	3.55	1.61	1.50		2.50
DF		4	4	4	4	4	DF	9	9	9	9		9
S		3.7	4.9	8.5	5.0	8.8	S	1.6	1.7	1.5	2.5		2.0
13. Benin-Burkina Faso							26. Kay Island						
C50	<0.1	0.60	<0.1	5.10	1.00	1.00	C50	0.30	0.17	0.04	0.20	ND	0.20
χ^2		2.50		0.80	0.90	1.70	χ^2	3.21	3.42	2.74	3.27		4.76
DF		4		4	4	4	DF	8	8	8	8		8
S		2.3		4.7	5.3	11.0	S	2.7	1.6	2.0	2.0		2.0

^a ND, not detected. A geometric mean (\bar{x}) is reported if samples were too few for a complete statistical evaluation.

Table IV. Values of Foliage-Air BCF for HCB, HCHs, and DDTs Calculated as Mass Ratio between Global Mean Concentrations (C50) in Foliage and Air, Compared to Experimentally Measured Values in Simulation Chambers (12)

	HCB	HCHs	DDTs
BCF (C50 ratio)	1.3×10^3	1.1×10^4	2.4×10^5
BCF (exptl)	1.9×10^3	4.6×10^3 (α) 3.4×10^3 (γ)	1.9×10^5 (p,p' -DDT) 1.3×10^5 (p,p' -DDE)

aspects of the global behavior of these molecules can be predicted from small-scale experiments and/or theoretical evaluations.

It could thus be suggested that vegetation can be used as an indicator of air contamination, although some sources of variability exist and cannot be controlled.

Possibly the use of old vegetation takes into account the different rates of absorption/release kinetics, but other pitfalls or sources of error (e.g., chemical reactions, translocation, local meteorological conditions) cannot be evaluated.

In the following paragraphs, some comments on the single substances will be presented.

Hexachlorobenzene (HCB). According to Atlas and Giam (4), HCB is, along with HCHs, one of the predominant chlorinated hydrocarbons in the marine atmosphere, with a relatively homogeneous distribution in the two

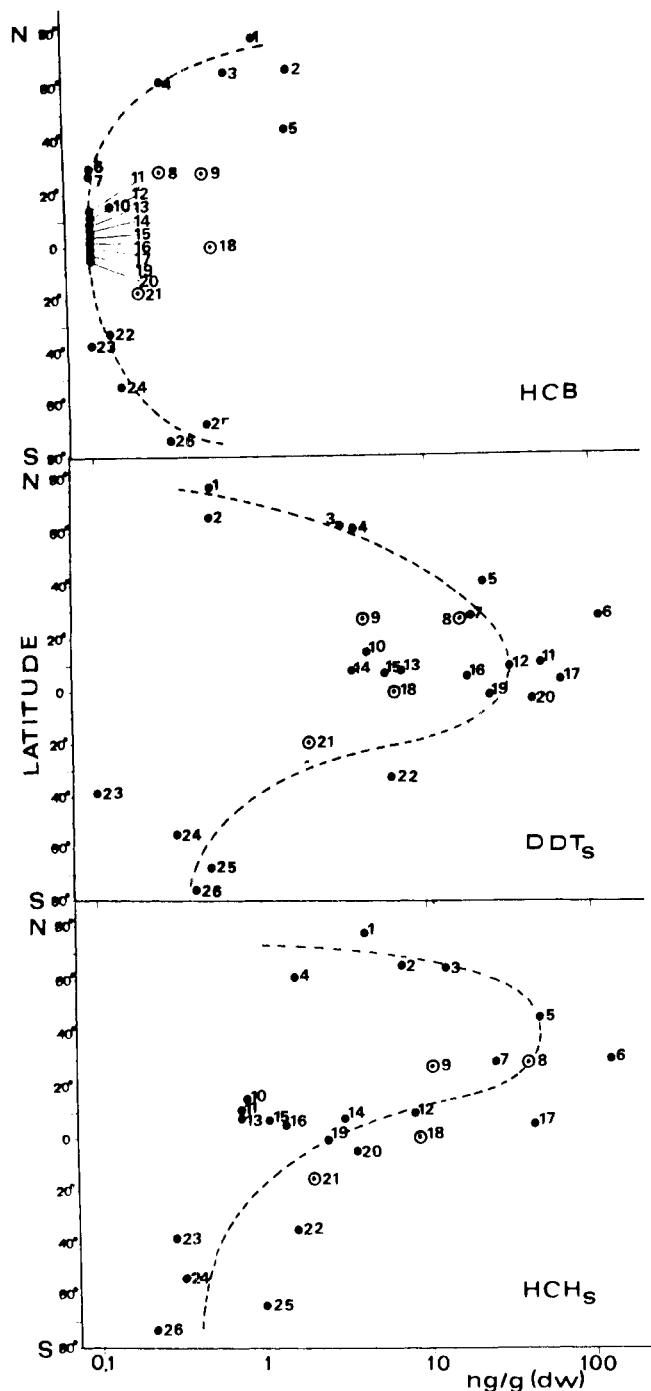


Figure 4. Distribution of HCB and sum of DDT and sum of HCH mean concentrations in the 26 sample sites as a function of the latitude. Circled points represent mountain sites.

hemispheres. In contrast, a high interhemispheric gradient has been suggested by Wittlinger and Ballschmitter (3) but this is based only on a limited quantity of data.

Differences in atmospheric distribution between compounds are related to differences in source strength and in atmospheric residence times. On the basis of its physicochemical properties, in particular its relatively high Henry's law constant, it is expected that HCB will have an atmospheric residence time longer than other chlorinated hydrocarbons. Consequently, Atlas and Giam (4) predicted and found a small interhemispheric gradient. This hypothesis has also been recently proposed in a wide literature survey carried out by GESAMP (5) and is confirmed by Figure 3, which indicates that atmospheric concentrations of HCB extend over a relatively small

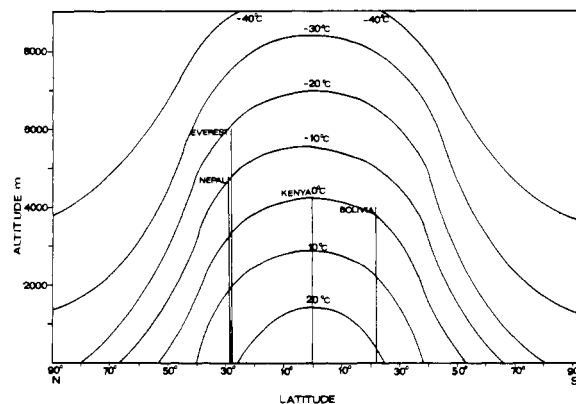


Figure 5. Global distribution of mean temperatures as a function of latitude and height. The four mountain sites considered in the present survey are indicated.

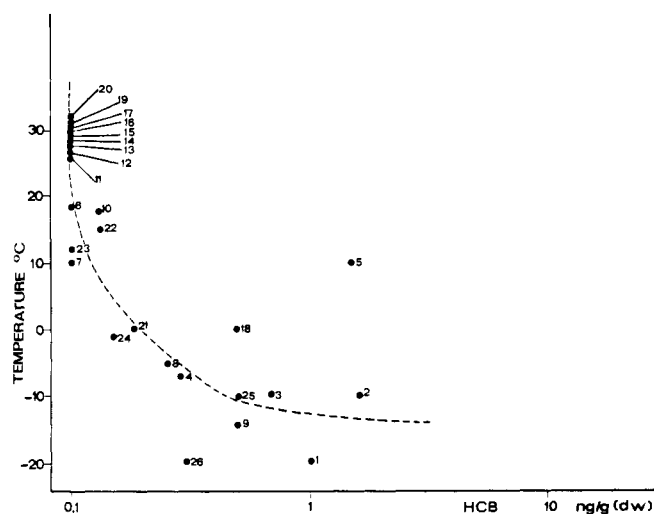


Figure 6. Relationship between HCB mean concentrations and mean temperature of the sampling sites.

range. Concentrations of HCB in plants verify this hypothesis, even if the differences among the slopes of the various molecules are less evident (Figure 2).

A better explanation of the variability of HCB concentrations in plants is given in Figure 4. From the figure it appears that, together with a slight difference between hemispheres, a difference between low and high latitudes is more evident. In tropical areas HCB concentrations in plants are always negligible and increase toward cold regions. Relatively high values in tropical or subtropical areas were found only in high-altitude samples (Nepal, Kenya, etc.).

On the basis of an approximate distribution of mean temperature in function of latitude and height (Figure 5) it is possible to find a good relationship between HCB concentrations and annual temperature averages, the only exception being Italian samples (Figure 6).

This trend can be explained by a "cold condenser" effect, particularly important with a volatile molecule such as HCB. These data indicate that the observed concentrations of HCB in the areas sampled in this survey are the result of a long-term distribution, regulated by global processes and physicochemical properties more than by direct contamination.

Italian data appear as outliers due to the fact that they derive from the only highly developed and industrialized temperate area included in the survey, where contamination due to use can be considered the prevailing process. HCB levels in Italian pines are comparable to those in plants from other developed countries (United States,

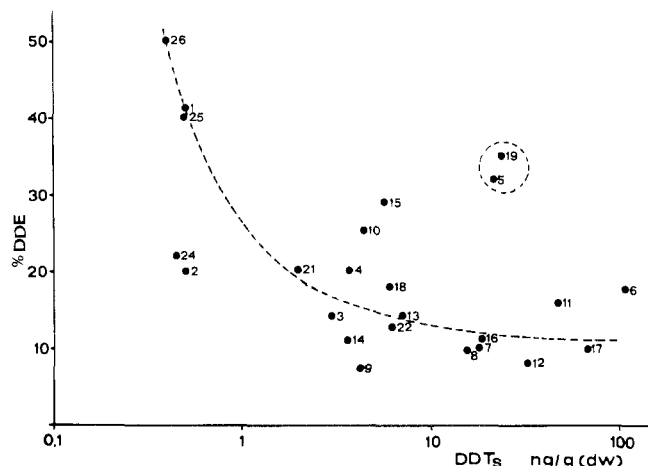


Figure 7. Relationship between DDT concentrations in foliage and the percentage of p,p' -DDE.

Yugoslavia) (15), but are not reported in this survey due to different sampling methodology.

DDTs. The most common DDT forms in the environment are p,p' -DDT, its isomer o,p' -DDT present in the technical product, and its degradation product p,p' -DDE, though in some cases other degradation products, such as DDDs, can be present at significant levels.

Total DDT introduced before the 1972 ban should exist primarily in the form of degradation products (mainly DDE) (36). However, DDT is still heavily used in several developing countries, accounting for the nonhomogeneous distribution of total DDT concentrations in the atmosphere (see slope in Figure 3). Current usage of DDT also affects concentrations measured in foliage. Higher concentrations were measured where an intensive use is still present or took place in the recent past.

In contrast to HCB, DDT plant concentrations are highest in tropical and subtropical areas (Figure 4).

In Figure 7 a relationship between the total amount of DDTs measured in foliage and the percent of DDE is evident. The highest values of DDT concentrations with low percentage of DDE are typical of areas where DDT is still in use in large amounts (e.g., India), whereas low levels of total DDTs correspond, in general, to high DDE percentages, and this can indicate long-range, indirect contamination. Only Italy and Kenya behave as outliers, being areas of high but not recent contamination.

Total DDT distribution is not related to temperature, unlike HCB. Nevertheless, for o,p' -DDT, a relationship with temperature was observed (Figure 8). This is in agreement with the physicochemical properties of the molecules (Table II) and in particular with the high Henry's law constant of o,p' -DDT, although very cold areas are not considered in the figure due to the low levels of DDTs that make unreliable the calculations of the percentage of the DDT forms.

Hexachlorocyclohexanes (HCHs). HCHs are used in the form of nearly pure γ isomer (lindane) or as technical product, a mixture of five isomers where the α form is the prevalent with an amount of ~55–80%. At present, the pure γ form is the most widely used but large amounts of the technical product are still produced and employed, mainly in the Far East (7).

HCHs show relatively high concentrations in the atmosphere and a gradient between the Northern and Southern Hemispheres has been observed (3–5).

Several authors indicated α -HCH as the major component of total HCH (1, 7, 8). Bidleman et al. (7) proposed two possible explanations: a long-range transport from

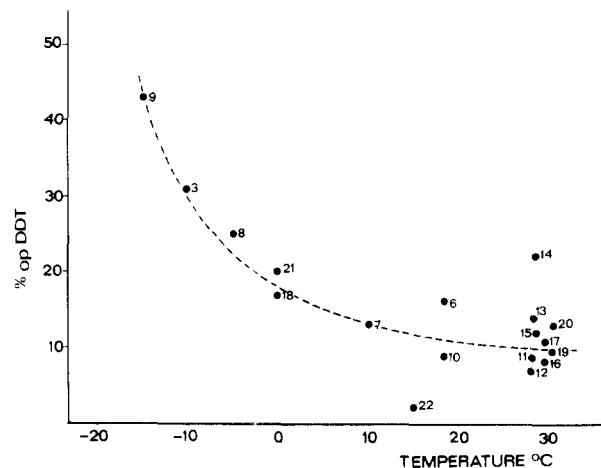


Figure 8. Relationship between the percentage of o,p' -DDT and the mean temperature of the sampling sites.

developing countries where the technical product is largely used, and an isomerization process from the γ to the α form.

On the other hand, Atlas and Giam (35) hypothesized that the ratio α -HCH/ γ -HCH is an indication of the age of an air parcel. A high α/γ ratio indicates older air. They observed that air masses with trajectories directly from Europe, where only the γ form is used, had an α/γ ratio of ~5/1, while background air had ratios near 50/1.

Foliage data measured in this survey show a relatively high C50 (Figure 2), comparable with the DDT value, and a flat slope, indicating a very wide range of concentrations.

The geographical distribution (Figure 4) confirms a gradient between Northern and Southern Hemispheres for total HCHs. The mean value (C50) of Northern samples is ~5 times higher than those of the Southern Hemisphere. The ratio between α and γ isomers confirms, with some exceptions, the prevailing role of α -HCH. Nevertheless it is very difficult to understand distribution patterns because the relative amounts of α and γ isomers are affected by at least two factors: the present use of the technical product or of the pure lindane, and the isomerization of γ - to α -HCH. The concurrence of those two factors can give very conflicting results. For example, the high α/γ ratios observed in some areas of Latin America (Amazonas, Delta Amacuro) can be assumed to be an indication of a strong use of technical product rather than of old contamination; in fact, the flat slopes observed in these extended areas seem to be an indication of recent and direct contamination. In contrast, the very low levels of α/γ ratio in some African areas indicate a recent use of the pure γ form. In conclusion, the levels of HCHs and the ratios between the two forms seem to be strongly affected by the present high use in different formulations rather than by long-range distribution processes and by the role of physicochemical properties, which are very similar for both isomers (Table II).

In the interpretation of the global distribution of persistent organic chemicals in vegetation based on physicochemical properties, it is important to use data from areas without relatively recent usage of the chemical. For HCB, only the Italian samples can be assumed not to have this characteristic. Thus, the main features of the observed distribution of HCB appear influenced more by long-range processes regulated by molecular properties and environmental phenomena (e.g., cold condenser effect) than by contamination due to use.

For HCHs and DDTs the problem is more complex due to the actual use of these molecules, in particular in de-

veloping countries from which most of the samples examined in this survey derive. Therefore only partial deductions can be made.

Conclusions

The present work and other literature on chemicals in vegetation indicate the following general conclusions: (a) there is a linear relationship between concentration of chemicals in foliage and in air (12), and the role of root translocation is, for the studied compounds, negligible (10); (b) chlorinated hydrocarbons can be detected in plant foliage from different species and the choice of the species is relatively irrelevant in relation to the aim of the investigation (15), especially when dealing with global distribution; (c) concentration in foliage is a suitable monitor of atmospheric contamination (11, 15, 31); (d) parent compound and metabolite ratios can provide information on the age of contamination (16, 36); (e) slopes of the frequencies of concentration (probits) within groups of samples (i.e., from the same geographical areas) can give indications of actual use and redistribution (17); (f) concentrations in lichens and mosses in Antarctica have been studied with the assumption that this area would have been the cleanest part of the world, being the farthest from the technological world (16); the findings however did not confirm this hypothesis (17), at least for certain substances (i.e., HCB); (g) chlorinated hydrocarbons distribute and cycle between air-water and air-soil by means of deposition-volatilization periods, with the so-called "grasshopper effect" (37); (h) according to literature data, substances with subcooled liquid vapor pressure (P_l) higher than 10^{-5} Pa tend to be distributed mainly in the vapor phase of the atmosphere, confirming the essential role of vapor movements in the global transport of these chemicals (38); (i) tropical areas have been identified, mainly due to climatic and meteorological reasons, more as contamination sources than as contamination receivers; this last role is more suited to the cold areas (cold condenser effect) (17).

Acknowledgments

We thank every person or organization contributing to the samples collection and B. Rordorf for providing unpublished data.

Literature Cited

- (1) Atlas, E. L.; Giam, C. S. *Science* 1981, 211, 163-165.
- (2) Tanabe, S.; Hidaka, H.; Tatsukawa, R. *Chemosphere* 1983, 12, 277-288.
- (3) Wittlinger, R.; Ballschmitter, K. *Fresenius J. Anal. Chem.* 1990, 336, 193-200.
- (4) Atlas, E. L.; Giam, C. S. In *The role of air-sea exchange in geochemical cycling*; Bouat-Menard, P., Ed.; NATO-ASI Series C 185; Reidel Publishing Co.: Dordrecht, The Netherlands, 1986; pp 295-329.
- (5) GESAMP, Joint Group of Experts on Scientific Aspects of Marine Pollution. *Rep. Stud.—GESAMP* 1989, No. 38, 1-111.
- (6) Tateya, S.; Tanabe, S.; Tatsukawa, R. In *Toxic contamination in large lakes*; Schmidtke, N. W., Ed.; Lewis Publishers: Chelsea, MI, 1988; Vol. III, pp 273-281.
- (7) Bidleman, T. E.; Wideqvist, U.; Jansson, B.; Soderlund, R. *Atmos. Environ.* 1987, 21, 641-654.

- (8) Patton, G. W.; Hinckley, D. A.; Walla, M. D.; Bidleman, T. F.; Hartgrave, B. T. *Tellus* 1989, 41B, 243-255.
- (9) Buckley, E. H. *Science* 1982, 216, 520-522.
- (10) Bacci, E.; Gaggi, C. *Bull. Environ. Contam. Toxicol.* 1985, 35, 673-681.
- (11) Ericksson, G.; Jensen, S.; Kylin, H.; Strachan, W. *Nature* 1989, 34, 42-44.
- (12) Bacci, E.; Calamari, D.; Gaggi, C.; Vighi, M. *Environ. Sci. Technol.* 1990, 24, 885-889.
- (13) Riederer, M. *Environ. Sci. Technol.* 1990, 24, 829-836.
- (14) Trapp, S.; Matthies, M.; Scheunert, I.; Topp, E. M. *Environ. Sci. Technol.* 1990, 24, 1246-1251.
- (15) Gaggi, C.; Bacci, E.; Calamari, D.; Fanelli, R. *Chemosphere* 1985, 14, 1673-1686.
- (16) Bacci, E.; Calamari, D.; Gaggi, C.; Fanelli, R.; Focardi, S.; Morosini, M. *Chemosphere* 1986, 15, 747-754.
- (17) Bacci, E.; Calamari, D.; Gaggi, C.; Biney, C.; Focardi, S.; Morosini, M. *Chemosphere* 1988, 17, 693-702.
- (18) Trevors, J. T. *Bull. Environ. Contam. Toxicol.* 1986, 37, 18-26.
- (19) Travis, C. C.; Land, M. L. *Environ. Sci. Technol.* 1990, 24, 961-962.
- (20) Helsel, D. R. *Environ. Sci. Technol.* 1990, 24, 1766-1774.
- (21) Hansch, C.; Leo, A. J. *Substituent constants for correlation analysis in chemistry and biology*; John Wiley: New York, 1979.
- (22) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of chemical property estimation methods*; McGraw-Hill Book Co.: New York, 1982.
- (23) Suntio, L. R.; Shiu, W. Y.; Mackay, D.; Seiber, J. N.; Giotfelty, D. *Rev. Environ. Contam. Toxicol.* 1987, 103, 1-59.
- (24) Worthing, C. R.; Walker, S. B. *The Pesticide Manual*, 8th ed.; The British Crop Protection Council: Lavenham, Suffolk, U.K., 1987.
- (25) Verschuere, K. *Handbook of environmental data on organic chemicals*, 2nd ed.; Van Nostrand Reinhold Co.: New York, 1983.
- (26) Morris, C. R.; Cabral, J. R. P. *Hexachlorobenzene: proceedings of an international symposium*; IARC Scientific Publication 77; International Agency for Research on Cancer: Lyon, France, 1986.
- (27) De Bruijn, J.; Busser, F.; Seinen, W.; Hermens, J. *Environ. Toxicol. Chem.* 1989, 8, 499-512.
- (28) Reishl, A.; Reissinger, M.; Hutzinger, O. *Chemosphere* 1987, 16, 2647-2663.
- (29) Villeneuve, J. P.; Holm, E. *Chemosphere* 1984, 13, 1133-1138.
- (30) Carlberg, G.; Baumann-Ofstad, E.; Drangholt, H.; Steinnes, E. *Chemosphere* 1983, 12, 341-356.
- (31) Villeneuve, J. P.; Fogelquist, E.; Cattini, C. *Chemosphere* 1988, 17, 399-403.
- (32) Schrmipff, E. *Water, Air, Soil Pollut.* 1984, 21, 279-315.
- (33) Guicherit, R.; Schulting, F. L. *Sci. Total Environ.* 1985, 43, 193-219.
- (34) Nakano, T.; Tasuji, M.; Okuno, T. *Chemosphere* 1987, 16, 1781-1786.
- (35) Atlas, E. L.; Giam, C. S. *Water, Air, Soil Pollut.* 1988, 38, 19-36.
- (36) Rapaport, R. A.; Urban, N. R.; Capel, P. D.; Baker, J. E.; Looney, B. B.; Eisenreich, S. J.; Gorham, E. *Chemosphere* 1985, 14, 1167-1173.
- (37) Mackay, D.; Paterson, S.; Schroeder, W. H. *Environ. Sci. Technol.* 1986, 20, 810-816.
- (38) Bidleman, T. F.; Billings, W. N.; Foreman, W. T. *Environ. Sci. Technol.* 1986, 20, 1038-1043.

Received for review January 23, 1991. Revised manuscript received April 18, 1991. Accepted April 22, 1991.