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Polychlorinated Biphenyls in Plant Foliage: Translocation or Volatilization from Contaminated Soils?

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Polychlorinated biphenyls (PCB's) are largely used (in electric capacitors and transformers, heat transfer systems, plasticizers, industrial fluids) because of their stability, inertness, and very good dielectric properties (Hutzinger et al. 1974). These chemicals are considered as xenobiotics, having been introduced into the biosphere after 1929, when their industrial production begun. More than 20 years ago, they were found in environmental samples collected for pesticide residue analysis (Jensen 1966). As a consequence of their persistence and high bioaccumulation potential, particularly in the case of the more chlorinated congeners, PCB's have been found in water, air, surficial soils, recent sediments, and biota (man included) in anthropized (Jensen 1983; Geyer 1984) as well as in remote areas (Atlas and Giam 1981; Subramanian et al. 1983). Because of this, and due to the toxicity of both commercial mixtures (WHO 1976; Suzuki 1978) and pure congeners (Goldstein 1980; Safe et al. 1982), in the seventies some governments of technically advanced countries regulated or banned the production and use of PCB's. However it was estimated that the world-wide production up to 1971 was about 1 million metric tons (WHO 1976; Jensen 1983). Moreover the production of PCB's is still going on in many countries.

Physical properties such as water solubility, vapour pressure, and Henry's - law constant (Mackay and Leinonen 1975) suggest that these compounds can easily reach the troposphere as vapour. Volatilized PCB's are little adsorbed by airborne particulate matter (Junge 1977; Eisenreich et al. 1981).

The potential of plant foliar tissues to take up PCB's as vapour has probably been underrated in some of the previous works (Iwata and Gunther 1976; Suzuki et al. 1977; Villeneuve and Holm 1984). Nevertheless recently Buckley (1982) reported

that the level of PCB's found in the foliage is mainly due to vapour transport from the soil, rather than to translocation through the plant.

This research has been planned to assess the influence of translocation on the concentration of PCB's in the foliage of different plant species.

MATERIALS AND METHODS

Two 60-cm-wide cubic glass boxes, mantained at a constant temperature by means of a warm water system in the bottom and continuously illuminated by 3x20 W True-Lite fluorescent tubes were used (Figure 1). The temperature was 24 °C at the bottom and 27 °C at the top, due to the lamps. The culture area was located in a glass tray to reduce the impact of air flowing in through a 3-cm-diameter hole placed near the bottom. Two other similar holes (Figure 1) and slight gaps between the box and its cover (which simply rested on the walls) guaranteed a sufficient air turnover. The air turnover time of each box, calculated from the decay of a tracer (α-hexachlorocyclohexane) was about 80 min. Since the air volume was 200 l, this means that the air input (and output) was 2.5 l min^{-1}.

A Pliocene sand, containing very low organic carbon (0.15 %, dry) was used as culture soil. It is classifiable as a 'fine sandy medium sand', according to Doeglas (1968). The sand was oven-dried (24 h at 80 °C) and, after cooling, equilibrated with benzene (1 l kg^{-1}, 3 d). Fortification was done with Fenclor 64 from Caffaro (Milan, Italy), very similar to the commoner Aroclor 1260 by Monsanto (USA), as shown in Figure 2. The nominal concentration of PCB in the sand was 500 mg kg^{-1}, dry basis. After the evaporation of the solvent, by a vacuum rotary evaporator, the average PCB concentration was 460 mg kg^{-1}, dry ($n = 5$; SD = 35).

Beans, broad beans, tomatoes and cucumbers were selected, the second two (2-3 weeks old, 5-10 cm high) from the market. The first two were seeded in our laboratory, after activation in water (1 h at 40 °C). Beans and broad beans were kept for 2 weeks at 24-25 °C (preliminary culture).

In a 'clean' area, away from the laboratory, five specimens of each of the species in question were grown in the same sand, pretreated with benzene, at room temperature. They were used as controls. The benzene was for pesticide residue analysis,

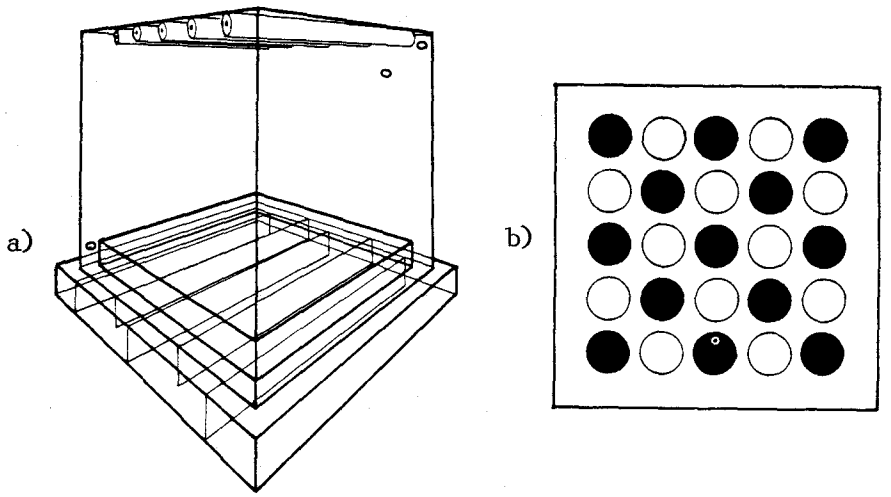

Figure 1. Schematic representation of the glass boxes (a) and of the alternation of vessels containing PCB-fortified sand (black circles) and 'clean' sand (white circles).

and the concentration of PCB's in the sand used was lower than 50 ng g^{-1} dry basis.

Box 1: broad beans and beans. Each plant was put into a separate cylindrical glass vessel, 4 cm high, 5 cm i.d., containing 40 g of either 'clean' sand or PCB-fortified sand. Vessels with 'clean' sand were alternated with those with fortified sand in a glass container inside the box, as indicated in Figure 1. The total fortified sand employed weighed 600 g. Water was supplied once a day to keep the sand moist.

Box 2: tomatoes and cucumbers were cultured as described above, using in the vessels either 50 g of 'clean' sand or 20 g fortified sand (on the top) and 30 g 'clean' sand. A total of 300 g PCB contaminated sand was used.

The sampling time was 28 d after the beginning of the treatment.

Analyses were carried out on air, sand, and plant-tissue samples. Air samples were collected using disposable Pasteur pipets packed with 0.3 g of Florisil, according to Giam et al. (1975), with slight modifications. PCB's were then eluted with 45 ml of n-hexane in a glass chromatographic column containing 0.3 g anhydrous Na_2SO_4. After concentration, the sample was injected into a Perkin-Elmer F 22 gas chromatograph equipped with on-column injector, Nickel-63 electron capture detector,

and a data station. Borosilicate glass-columns 2 m x 2 mm i.d., silane treated, packed by GP 4% SE-30 6% SP-2401 on 100/120 mesh Supelcoport were used. The carrier gas was argon with 5% methane; gas flows: 60+40 (as scavenger) ml min^{-1}. Injector, oven and detector temperatures were 210, 200 and 280 °C.

Plant tissue and sand samples were dried overnight (5-15 % moisture content) in an oven at 60 °C (plant tissues) or at room tmperature (sand). Residual water was measured on subsamples (24 h at 105 °C). Previous tests have shown that in plant leaves, kept at 70 °C for 7 d, no significant PCB loss occurs. Extractions were carried out overnight in Soxhlet apparatus, using n-hexane. The clean-up procedure was the following: sulfuric acid treatment (Murphy 1972) and Florisil chromatography, as for air samples. Gas-chromatographic conditions: as before.

PCB quantification: sand and root samples were compared to the Fenclor 64 reference solutions, since the peak pattern of all three are very similar (Figure 2). It was assumed that no chemical transformation occurred during the experiment. To calculate the PCB concentration in air and foliage samples the perchlorination method suggested by Stratton et al. (1979) was tried. Results were unsatisfactory, except for pure standard PCB mixtures. Therefore the following method was used for the calculation: three peak heights were chosen with 84, 146 and 280 relative retention times with respect to p,p'DDE (as 100), and corresponding to certain 5-, 6-, and 7-chlorobiphenyls (Hutzinger et al. 1974). The per cent weight of the components of each peak was assumed to be equal to the values reported by Webb and McCall (1973) for the same peaks from an Aroclor 1260 mixture: 4.7 % for the peak 84, 14.1 % for 146 and 11.0 for 280.

RESULTS AND DISCUSSION

In the controls the PCB level found in the root and foliage, collected after 28 d of main culture, was lower than 50 ng g^{-1}, dry weight.

No evidence of toxicological effects due to the PCB treatment was observed in the plants grown in the boxes. A few plants (discarded), both in PCB-fortified sand and in 'clean' sand, did not thrive, probably due to the benzene residues in the sand.

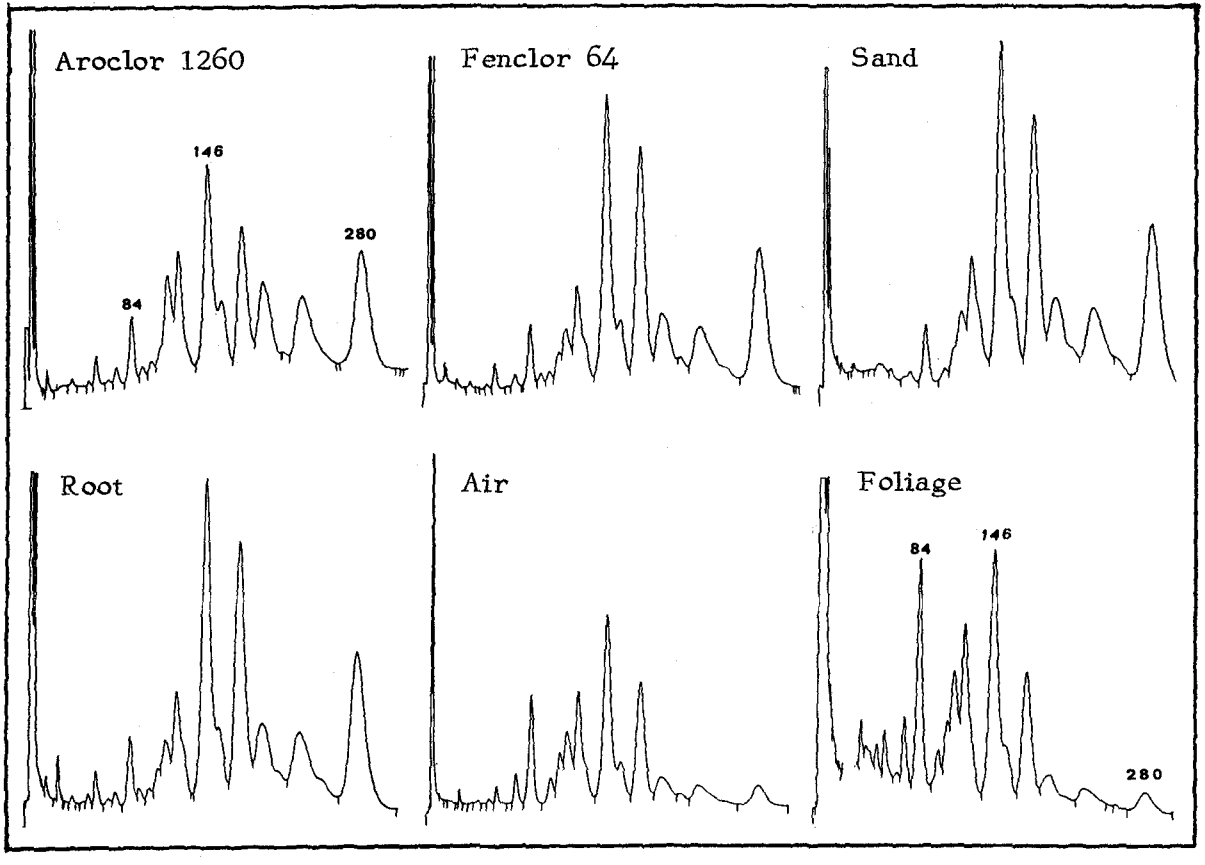

Figure 2. Chromatograms of reference PCB mixtures and of the analyzed materials. Numbers on the top indicate the p,p'DDE relative retention times of the peaks used for PCB quantification.

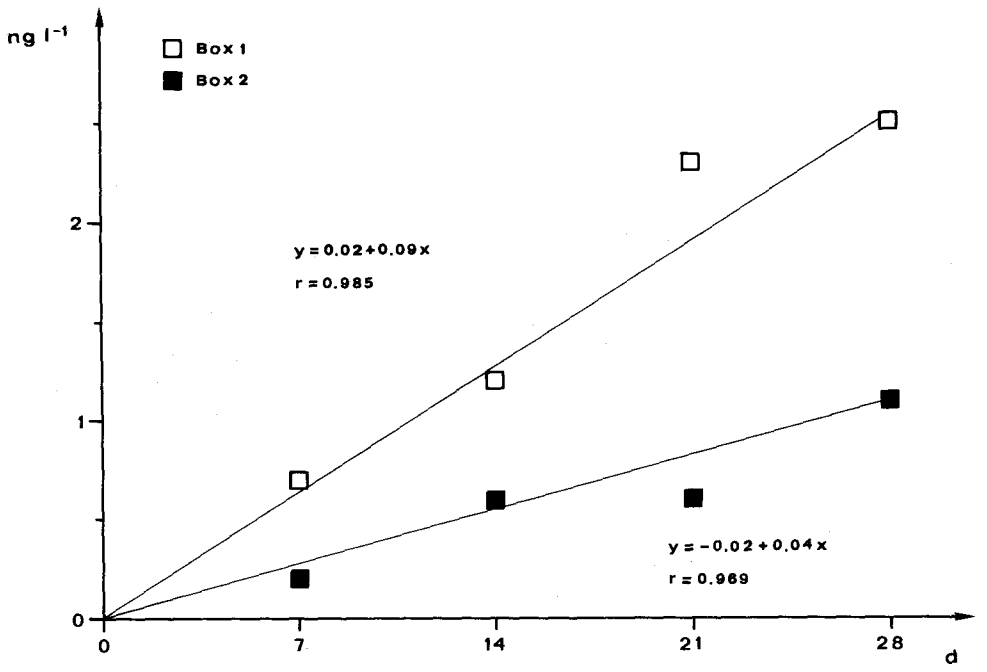

Figure 3. Trends of PCB concentration in the air of the boxes.

The PCB peak pattern in sand and root samples was very similar to that of Fenclor 64, while in the air and foliage a remarkable displacement to the left (higher 'early' peaks) was obtained (Figure 2). This is in agreement with the Haque et al. (1974) findings on the vapour behavior of Aroclor 1254. A similar displacement of the PCB peaks is reported by Suzuki et al. (1977) for soybean sprouts cultured in sand fortified with Aroclor 1254.

Tha air turnover time being constant, the trend of the PCB concentration in the air of the boxes (Figure 3) shows that the volatilization rate of these chemicals increases regularly during the experiment. This was an unexpected result, as volatiliza-

Table 1. Concentrations of PCB ($\mu g\, g^{-1}$, dry basis) in the leaves of plants grown in PCB-fortified sand (F) and in 'clean' sand (C), after 28 d of culture.

	broad bean			bean			tomato			cucumb.	
	$\bar{x}$	n	SD	$\bar{x}$	n	SD	$\bar{x}$	n	SD	$\bar{x}$	n
F	26.4	6	4.0	42.6	6	10.6	24.3	6	8.7	13.8	1
C	20.2	6	7.8	47.1	6	9.7	22.3	6	4.2	11.8	1

tion is characterized by 0-order kinetics. In similar experiments (in progress) with lindane and α-hexachlorocyclohexane treated sands, a steady-state of the pollutant level in the air is reached in less than 2 d and mantained for several weeks. A possible explanation lies in the presence (in the sand) of residues of incompletely evaporated benzene, which may reduce the fugacity of PCB's from the sand. If so, as the experiment progresses and the benzene evaporates, the volatilization rate of PCB's would increase. Probably more volatile solvents, like n-hexane, can reduce such a complication. The PCB vapour level found in the air of each box at a given time appears to be proportional to the quantity (or evaporating surface) of the fortified sand used.

Concentrations of PCB found in the root of tomatoes grown in the contaminated sand for 28 d were 105, 132, and 168 $\mu g\, g^{-1}$, dry basis, but the possibility of a translocation of PCB through the plant tissues seems very slight: in Table 1 it is shown that the PCB concentration in the leaves of the plants is not significantly dependent on the contamination level of the soil where they were grown. And this is the case using a soil with a high PCB fugacity (0.15 % organic carbon) and a PCB mixture characterized by 'low' volatility (60 % chlorine content).

Probably the PCB found in the root is stopped at the root peel level, the mobility of these chemicals through plant tissues being very low (Iwata and Gunther 1976; Weber and Mrozek 1979).

The difference in the PCB peak pattern between sand and foliage (Figure 1) demonstrates that the levels found in plant leaves are not due to contamination by soil particles, offering further confirmation that the vaporization from the polluted soil is the main route for the foliage contamination.

Small green-houses of the sort we employed are a low-cost tool for similar studies, kinetics, and modelling of pollutants' environmental fate.

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