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DDT Concentrations in Soils of Brazzaville, Congo

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DDT is among the 12 persistent organic pollutants (POPs) to be eliminated worldwide under the Stockholm Convention (UNEP, 2001). However, due to the more important threat from endemic and epidemic diseases such as malaria compared to that posed by the pesticide hazards, DDT is still used in many tropical and subtropical regions, including Africa. DDT use for vector disease control is permitted under the Stockholm Convention in accordance with World Health Organization (WHO) guidelines. The position of WHO (2005) is that there will be a continued role for DDT in combatting malaria, and restrictions on DDT use for public health purposes should be accompanied by technical and financial measures to ensure that control is maintained by alternative methods.

DDT residues in African countries have been reported in air (Karlsson et al., 2000; Larsson et al., 1995; Ngabe and Bidleman, 1992), plants (Calamari et al., 1991), fish (Berg et al., 1992; Kidd et al., 2000; Lalah et al., 2003; Mbongwe et al., 2003; Mhlanga et al., 1990), reptiles (Lambert, 1993) and human milk (Bouwman et al., 1994; Chikuni et al., 1997).

Despite the continual usage of DDT in Africa, there is a lack of data for soils. DDT and other chlorinated pesticides contaminate soil during application for agriculture and insect control operations, spray drift to non-target sites, and atmospheric deposition. The soil is a reservoir for these pesticides, and long after their use is stopped, soil residues can be a continuing source of atmospheric contamination through volatilization (Bidleman and Leone, 2004; Finizio et al., 1998; Meijer et al., 2003; Spencer et al., 1996). Dissipation of DDT and other chlorinated pesticides from soil is faster in tropical compared to temperate conditions due to increased volatilization and degradation (Khan, 1994; Lalah et al., 2001; Tanabe et al., 1991; Yeadon and Perfect, 1981).

We sampled ambient air in Brazzaville, Republic of Congo, in 1989 and found total DDT concentrations ranging from 1.5 to 3.8 ng m^{-3} and averaging 2.8 ng m^{-3}. Other chlorinated pesticides were much lower (ng m^{-3}): lindane 0.39, α-hexachlorocyclohexane (α-HCH) 0.034 and chlordanes (sum of cis-chlordane, trans-chlordane and trans-nonachlor) 0.027 (Ngabe and Bidleman, 1992). This work was aimed at determining the levels of DDT compounds in soils from Brazzaville as a step to building a data base on DDT in tropical African soils.

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MATERIALS AND METHODS

Soil samples were taken in various locations in the city of Brazzaville (4.14° S, 15.14° E) in 1999. The samples were collected from farming areas (~ 50 ha), dirt areas along city streets and yards of schools and office buildings. Descriptions are given in Table 1. The samples were collected from the surface to 15 cm using a metal trowel, packed in aluminum foil and sealed in air-tight polyethylene bags for shipment to the laboratory in Canada. Once received, they were frozen at -20 °C until analysed. The organic carbon content of the soils was determined by combustion after acidifying to remove carbonates. For pesticide analysis, the following procedures were used (Harner et al., 1999): aliquots of soil (10-15 g wet weight) were weighed out exactly into a small beaker, mixed with anhydrous sodium sulphate and then ground until fine, grainy consistency was achieved. The mixtures were transferred to 150 ml ceramic thimbles and soxhlet extracted overnight using dichloromethane. Prior to extraction, the deuterated compound [$^2H_8$]-p,p'-DDT was added as a surrogate to monitor analytical recovery. The extracts were concentrated and transferred into hexane by rotary evaporation followed by blowing down with a gentle stream of nitrogen to 1 ml. Samples were purified by column chromatography on a 1-g neutral aluminum oxide column (6% added water), eluted with 20 ml 5% dichloromethane in petroleum ether. If required, extracts were shaken with 18 M sulphuric acid for additional cleanup. Eluates were blown down into isooctane to a final volume of 1 ml for analysis and mirex was added as an internal standard.

Quantitative analysis was done by gas chromatography with electron capture detection (GC-ECD) using a Hewlett-Packard 5890 instrument and a DB-5 capillary column (60 m x 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Rancho Cordova, CA, U.S.A.). Sample volumes of 2 μL were injected splitless (split opened after 0.5 min). Oven program: 90 °C (hold 1 min), 20 °C min^{-1} to 160 °C, 2 °C min^{-1} to 260 °C (hold 10 min). Other conditions were: He carrier gas at 50 cm s^{-1}, injector 250 °C, detector 300 °C. Analytes were quantified against dilutions of a 20 compound standard pesticide mixture using HP Chemstation software. The deuterated p,p'-DDT eluted slightly earlier and was resolved from unlabelled p,p'-DDT in the soil samples. The quantitation limit for soil residues (0.1 ng g^{-1}) was set by the lowest concentration injection standard.

Chiral analysis of o,p'-DDT was done by GC-electron capture negative ion mass spectrometry (GC-ECNI-MS) using a Hewlett-Packard 5890 GC-5898B MS Engine and methane at a nominal pressure of 1.2 Torr. Enantiomer separations were done on a BGB-172 capillary column (20% tert-butylsilylated β-cyclodextrin in OV-1701 (30 m x 0.25 mm i.d., 0.25 μm film thickness, BGB Analytik AG, Switzerland). Sample volumes of 2 μl were injected splitless (split open after 1 min). Operating conditions were as described by Wiberg et al. (2001). Ions 246 and 248 were monitored for o,p'-DDT. For a satisfactory analysis, the ion ratio for samples was required to be within the 95% confidence limits for standards (Bidleman and Leone, 2004). The elution order of o,p'-DDT enantiomers on the BGB-172 column is reported as (–), (+) (Buser and Müller, 1995). This was confirmed by running Standard Reference Material 1688 cod

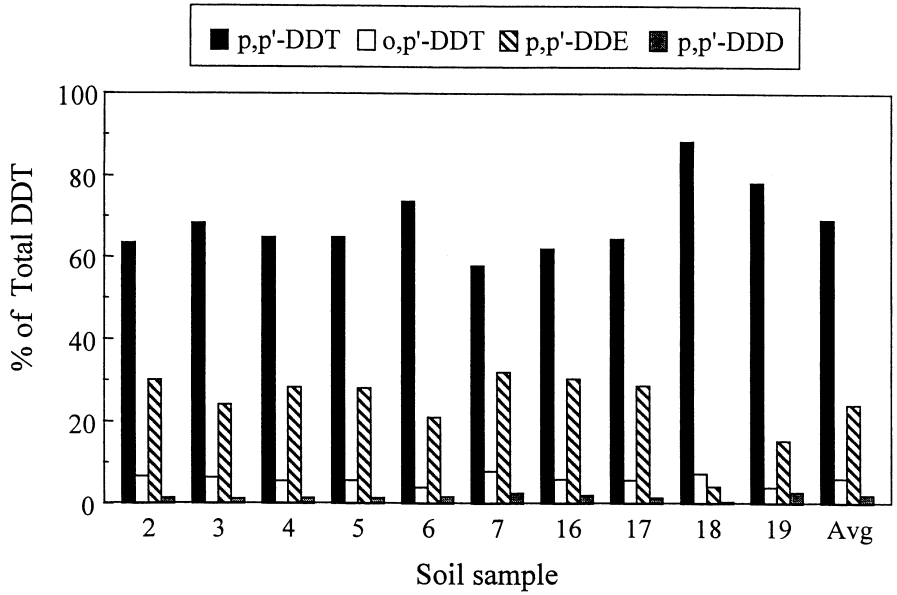

Figure 1. Distribution of DDT compounds in soils with detectable residues.

liver oil (National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.), which is enriched in the (+) enantiomer (Hoekstra et al., 2005).

All solvents and reagents used were chromatographic or analytical quality. Solvents were from EMD Omnisolv® (Gibbstown, NJ, U.S.A). Aluminum oxide (neutral alumina, 6% deactivated 0.063 - 0.30 mm EM Science, Darmstadt, Germany) and granular anhydrous sodium sulphate (EM Science) were baked at 400 °C overnight. The recovery surrogate [$^2H_8$]-p,p'-DDT was obtained from Cambridge Isotope Laboratories (Andover, MA, U.S.A.). Unlabelled standards were obtained from AccuStandard (New Haven, CT, U.S.A.).

RESULTS AND DISCUSSION

Four DDT compounds were quantified in the soils: p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD, and concentrations on a dry weight basis are reported in Table 1. ΣDDT ranged from <0.1 – 266 ng g^{-1}. Soil 5 was analysed in triplicate and soils 3 and 16 were analysed in duplicate. Pooled relative standard deviations from these replicate analyses were 14%, 33%, 28% and 22% for the four DDT compounds. The average recovery of the deuterated p,p'-DDT surrogate was 82% with a standard deviation of 16% (n = 22). Other organochlorine pesticides (lindane, chlordanes) were sought, but were below 0.1 ng g^{-1}.

The highest ΣDDT residues, ranging from 166–266 ng g^{-1}, were found in three farming areas (samples 16, 17 and 18) and a yard near a university building (sample 7). Residues at the fourth farm (sample 19) and office building yards in the downtown area (samples 2-6) were lower, ranging from 29–88 ng g^{-1}. None of the soils from streets (samples 9–15), nor a school yard soil (sample 1) contained

Table 1. DDT in soils of Brazzaville, Congo, ng g^{-1} dry weight

	location name	land use	% organic carbon	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-DDD	Sum DDT	% p,p'-DDT[a]	DDT/DDE[b]	EF o,p'-DDT
1	Ecl. Normale Superieur	school	0.17	ND[c]	ND	ND	ND	ND			NA[c]
2	Centreville 1	office	1.8	36	3.7	17	0.79	57	63	2.12	0.541
3	Centreville 2	office	NA	60	5.7	21	1.1	88	68	2.84	0.502
4	Centreville 3	office	1.1	39	3.3	17	0.85	60	65	2.29	0.497
5	Centreville 4	office	0.21	37	3.2	16	0.82	57	65	2.31	0.504
6	CCA	office	NA	42	2.2	12	0.89	57	74	3.50	0.489
7	Faculté des Sciences	univ.	1.1	96	13	53	4.2	166	58	1.81	NA
8	Intendance	street	0.22	ND	ND	ND	ND	ND			NA
9	Ouenzé	street	0.54	ND	ND	ND	ND	ND			NA
10	Talangai	street	0.40	ND	ND	ND	ND	ND			NA
11	Moungali	street	0.37	ND	ND	ND	ND	ND			NA
12	Plateaux 15 ans	street	0.45	ND	ND	ND	ND	ND			NA
13	Mikalou	street	0.40	ND	ND	ND	ND	ND			NA
14	Mbouale	street	0.53	ND	ND	ND	ND	ND			0.502
15	Ntsieme	street	0.62	ND	ND	ND	ND	ND			0.502
16	Cent fils 1	farm[d]	2.9	149	14	73	4.7	241	62	2.04	0.500
17	Cent fils 2	farm[d]	NA	171	15	76	3.7	266	64	2.25	NA
18	Kombé 1	farm[e]	NA	159	13	7.4	0.89	180	88	21.49	0.493
19	Kombé 2	farm[e]	NA	23	1.2	4.5	0.80	29	78	5.11	0.502
mean of positive samples				81	7.4	30	2.0	120	69		
s.d. of positive samples				58	5.6	27	1.7	86	9.0		

a) 100 x p,p'-DDT/sum-DDT

b) p,p'-DDT/p,p'-DDE

c) ND = not detected, <0.1 ng g^{-1}; NA = not analysed.

d) family farm

e) government farm

detectable DDT residues. The undetectability of the DDTs in street soils may be due to the fact that such areas were sometimes covered by clean sands to keep the mud down. It was also generally the case that DDTs were not detected in soils with low percentages of organic carbon (samples 1 and 9–15, 0.17–0.62%), although 57 ng g^{-1} ΣDDT was found in sample 5 with 0.21% organic carbon. Other soils with measureable DDT residues had organic carbon contents ranging from 1.1–2.9%, but a meaningful correlation could not be established because organic carbon was not determined in all the soils. It may be that DDT residues in the soils were more related to land use than carbon content.

Table 2. DDT in urban soils, ng g^{-1} dry weight

location	land use	year	samples	Sum-DDT[a] range	Sum-DDT mean ± s.d.	reference
Brazzaville, Congo	streets	1999	8	ND[b]	ND	this study
Brazzaville, Congo	agriculture	1999	4	29-266	179±106	this study
Brazzaville, Congo	school and office yards	1999	7	ND-166	69±50	this study
Beijing, China	not reported	2003	30	7.2-244	57±55	Li et al., 2005
Tianjin, China	not reported	2001	188	0.7-972	56±134	Gong et al., 2005
Taipei, Taiwan	urban - gardens	1990	3	6.9-25	13±10	Thao et al., 1993
Taiwan	roadside	1990	6	5.0-31	17±12	Thao et al., 1993
Thailand	roadside	1988	2	2.4-4.9		Thao et al., 1993
Katowice, Poland	urban-industrial	1994	9	23-260	110±89	Falandysz et al., 2001
Krakow, Poland	urban-industrial	1994	15	4.3-1200	259±624	Falandysz et al., 2001
Romania	urban-industrial	NR[b]	20	NR	105±142	Covaci et al., 2001

a) Includes three or more of: p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD.
b) ND = not detected, <0.1 ng g^{-1}; NR = not reported.

ΣDDT in Brazzaville soils are compared to those in other urban areas in Table 2. Reported concentrations in urban soils vary by 1-2 orders of magnitude, even within a single study. This was also found for agricultural soils in the U.S.A. (Aigner et al., 1998; Bidleman and Leone, 2004; Kannan et al., 2003). Mean concentrations in Brazzaville are of the same magnitude as other reported results.

Proportions of the four DDT compounds in soils with measureable residues are shown in Figure 1; p,p'-DDT accounted for 58-88% (mean 69±9%) of ΣDDT. Ratios of p,p'-DDT/p,p'-DDE (DDT/DDE) ranged from 1.8–3.5 at most locations, but higher ratios of 21 and 5.1 were found at the two Kombé farms (samples 18 and 19). The median DDT/DDE ratio was 2.3. Enantiomer fractions of o,p'-DDT, EF = area of (+)/[(+) + (−)] enantiomers, were determined for ten soils, including two street soils (samples 14 and 15) for which concentrations of o,p'-DDT were below the quantitation limit. This was possible because sample extracts were concentrated to a lower volume (~100 μL) for enantiomer determinations. EFs for nine soils ranged from 0.489–0.504, and the EF for one soil (sample 2) was 0.541 (Table 1). The mean and 95% confidence limits for the EF of a racemic o,p'-DDT standard were 0.499 ±0.011. Thus, only sample 2 had an o,p'-DDT EF which was significantly different from racemic. Enantioselective degradation of o,p'-DDT in soils is ambivalent, with preferential loss of the (+) enantiomer, the (−) enantiomer and racemic residues occurring with about equal frequency (Aigner et al., 1998; Bidleman and Leone, 2004; Wiberg et al., 2001).
DDT is degraded in soil by chemical and microbial processes to the persistent and toxic metabolites DDE and DDD (Lalah et al., 2001). Various workers report total DDT in different ways. Total DDT usually includes p,p'-DDT, p,p'-DDE and p,p'-DDD, and sometimes the o,p'-isomers. The ratios of p,p'-DDT to p,p'-DDE (DDT/DDE), or p,p'-DDT/ ΣDDT are often used to roughly estimate the age of

residues in the environment; high ratios imply more recent DDT usage. DDE is more persistent than DDT and may become predominant in soils which have not been exposed to new DDT sprayings (Boul et al., 1994). The proportions of DDTs and their breakdown products vary greatly in soils and are affected by soil management practices such as tilling, fertilizer additions, the presence of aerobic or anaerobic conditions and reactions with clay minerals (Boul et al., 1994; Edwards, 1966; Lalah et al., 2001; Spencer et al., 1996). Some soils retain a high proportion of parent DDT for decades after the end of DDT applications because they lack the microbial capability for DDT degradation (Hitch and Day, 1992).

Ratios of DDT/DDE in agricultural soils of the U.S.A. ranged from 0.04–2.4 in the southern states (Bidleman and Leone, 2004; Kannan et al., 2003) and 0.4–6.6 in the midwestern states (Aigner et al., 1998) with median values of 0.45 and 1.4 in the two regions. Similar statistics for DDT/DDE in soils near the Guanting Reservoir, Beijing, China were 0.20–4.3 and 0.78 (Hong et al., 2004). The degradation product p,p'-DDE in Chinese cities accounted for an average 61% of ΣDDT in Beijing (Li et al., 2005), but only 34% in Tianjin, where p,p'-DDT was most prominent (DDT/DDE = 1.46) (Gong et al., 2005). Levels of DDTs in soils from Polish cities decreased in the order p,p'-DDT > p,p'-DDE > p,p'-DDD, with an average DDT/DDE ratio of 1.6 (Falandysz et al., 2001), whereas in Romanian urban areas p,p'-DDT accounted for 48% of ΣDDT (Covaci et al., 2001). In soils from gardens and roadsides in Thailand and Taiwan, p,p'-DDT accounted for 15-65% (mean 36±16%) of ΣDDT (Thao et al., 1993).

Given this variability, it is difficult to determine if ongoing usage of DDT is contributing to residues in Brazzaville soils. The high ends of the DDT/DDE ratio ranges reported for China and the U.S.A. (see above) indicate that parent DDT can predominate in some soils, even though DDT usage has been discontinued for 2-3 decades. However, p,p'-DDT predominated in all Brazzaville soils with detectable residues and nine of ten soils examined contained racemic o,p'-DDT. This suggests that the residues are due in part to recent use of DDT.

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