ORGANOCHLORINATED PESTICIDE LEVELS IN AGRICULTURAL AND FOREST SOIL FROM SÃO PAULO STATE, BRAZIL

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Introduction

Organochlorinated pesticides (OCP) were once widely used in agriculture and were first registered in Brazil in 1946[1]. In the following years, the use for plant protection formulations increased rapidly. In the 1970´s, following international concern about the safety on such chemicals, Brazil restricted their production, trade and use through the publication of a series of regulations. This was followed in 1985 by Ministry of Agriculture regulation MAPA 329/85 prohibiting the trade, distribution and use of OCP in agriculture, except in declared emergencies[1].

Although most of the OCP have been prohibited for the agricultural use in Brazil since 1985, they are still found in soil samples[2].

In Brazil, for the evaluation of soil quality monitoring activities there is a national orientative guideline[3]. The guiding values are concentrations of chemicals that provide guidance on the condition of soil and groundwater quality and amendments imposed by anthropic action. São Paulo State has established guideline values for chemical substances in soil and groundwater, were are defined soil quality reference (QRV), preventive values (PV) and intervention values (IV) since 2001[4]. The QRV is the background concentration of chemicals in soil or ground water and it was considered only the group of naturally occurring inorganic substances based on geochemical processes. Anthropic organic compounds were considered naturally absent and therefore QRV was not applicable, but it is known that POPs are ubiquitously distributed and are present in air, sediment and biota.

This study represents a regional soil quality data collection to improve the knowledge of the soil quality in São Paulo State and in the future subsidize the reviewing process of the soil quality orientative guideline in the State.

The compounds included in this study were aldrin, endrin, dieldrin, chlordane (cis and trans), endosulfan (α, β and sulphate), heptachlor, heptachlor epoxide, hexachlorobenzene (HCB), DDT (and DDE, DDD), mirex, toxaphene, α and β hexachlorocyclohexane (HCH), lindane and methoxychlor.

Materials and methods

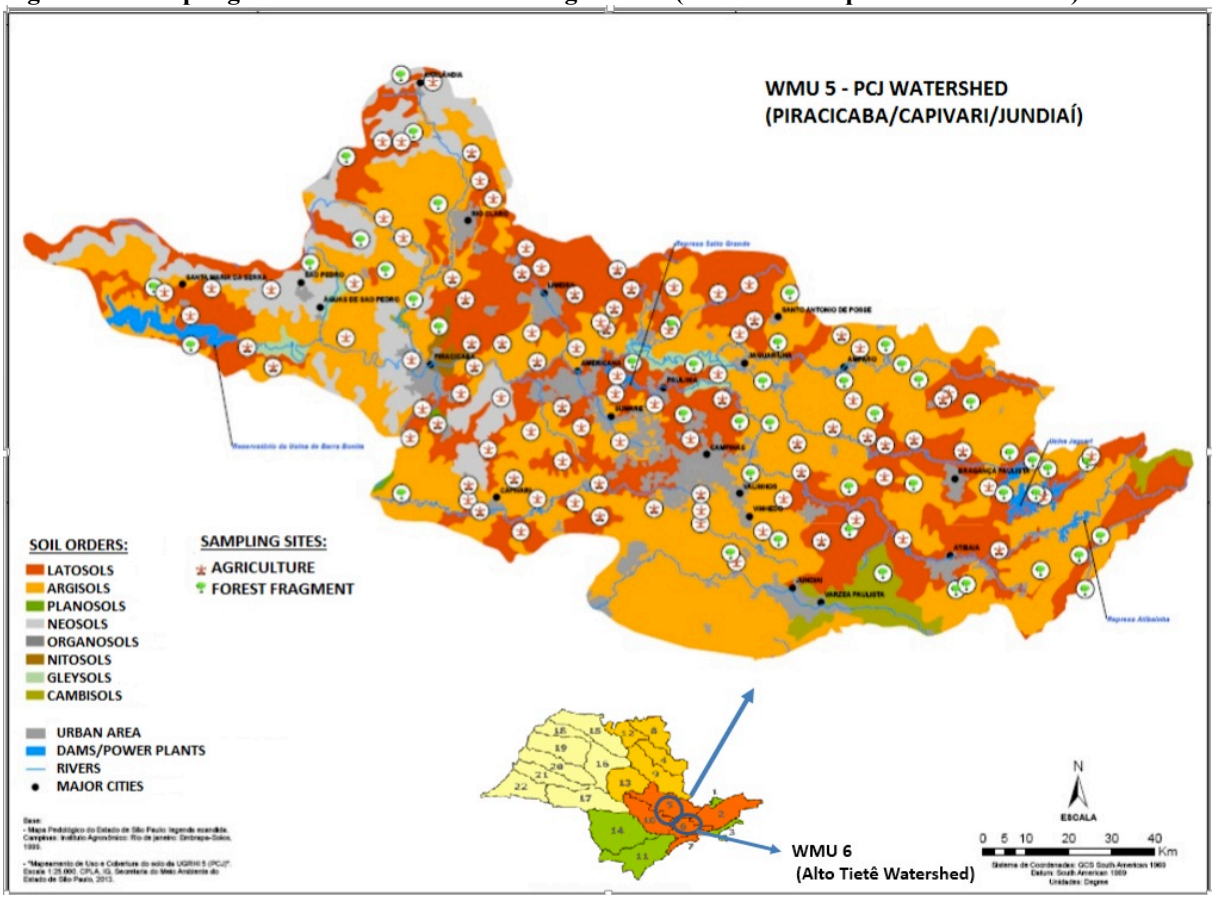
The area chosen for the study is one of the 22 Watershed Management Units (WMU) of São Paulo State, the WMU #5 (PCJ). This area is considered priority for this study to present complex and diversified industrial structure and provision of services, besides maintaining significant areas with agricultural use and forest fragments. The WMU #5 or PCJ (Piracicaba, Capivari and Jundiai) watershed consists of basins of Piracicaba (11,320km^2), Capivari (1,570km^2) and Jundiai (1,150km^2) rivers. The basin of these rivers covers 57 municipalities and, according to the IBGE (Brazilian Institute of Geography and Statistic) projection for 2012, comprises over 12% of the state population, of which 96% lives in urban areas. Traditionally agricultural (mainly sugarcane and coffee plantations), the region has become in recent decades a major industrial centers in the country.

Composite soil samples were collected at a depth of 0 to 20 cm, with stainless steel auger, homogenized and packed in glass jars. Two types of land use were considered for this study: agricultural and forest fragments. The total of 139 samples (93 samples from agricultural area and 46 samples from forest fragment) were collected during 2007 and 2012.

The OCP analysis was performed according to the method US EPA 8081B[5]. The soil samples were spiked with tetrachloro-m-xylene and decachlorobiphenyl as surrogate standards and extracted with n-hexane: acetone (1:1) in a Soxhlet extractor during 24h. The extract were cleaned up by gel permeation and then by silica gel column. The final extracts were analyzed in an Agilent 5890 and/or 7890 model gas chromatography/single electron capture detector (GC/ECD) and dual micro electron capture detector (GC/ECD/ECD). The GC/ECD was fitted

with a CPSil 8CB capillary column (60m x 0.25mm id x 0.25 µm film thickness) and/or a VF-Xms column (60m x 0.25mm id x 0.25 µm film thickness). The GC/ECD/ECD was fitted with a DB-5ms capillary column (60m x 0.25mm id x 0.25 µm film thickness) and a capillary column DB-1701 (60m x 0.25mm id x 0.25 µm film thickness).

Figure 1 – Sampling Sites: Watershed Monitoring Unit #5 (Piracicaba/Capivari/Jundiai -PCJ)



Results and discussion

The results of OCP analysis in agricultural and forest fragment soils from PCJ watershed are summarized in Table 1 and Table 2, respectively. The results from previous study at Alto Tiete watershed, with the biggest industrial park of the state, were included at the Table 1 and Table 2 for comparison purpose. The results were compared to the PV and agricultural IV.

Among 139 samples analyzed at PCJ watershed, were found at least one of OCP in 30 samples (21.6%), 26 of which (18.7%) from agricultural soils and 4 (2.88%) from forest fragment soils.
The compounds detected were aldrin, chlordane, dieldrin, endrin, DDT and its metabolites (DDE/DDD), endosulfan, heptachlor epoxide, HCB, lindane, α-HCH, methoxychlor and mirex at agricultural area, and heptachlor epoxide, DDE and metoxichlor at forest fragment area.

The DDT and its metabolites DDE and DDD were the most frequently OCP detected in agricultural areas. DDT and DDE concentration exceeded the PV values in six samples (roses, corn, horticulture, peach and citrus cultures). Aldrin, dieldrin and endrin were detected in agricultural area and concentration were higher than PV

for dieldrin (1 roses and 2 corn cultures) and endrin (1 roses and 1 sugarcane cultures). Hexachlorobenzene was found in four samples from agricultural area (3 sugarcane, 1 citrus cultures), all of them below PV. Lindane (γ-HCH) was found in three samples from agricultural area (citrus, eucalyptus and corn), two of them with the concentration higher than PV (citrus and corn). α-HCH was found in one sample from agricultural area (citrus) in concentration higher than agricultural IV.

Table1 – Concentration of OCP quantified in soil samples collected from agricultural area at Alto Tiete watershed (n=48) and Piracicaba/Capivari/Jundiai (PCJ) watershed (n=93)

OCP (□g Kg^{-1} d.w.)	PV	IV Agricultural	Alto Tiete		PCJ	
			Results >LOQ	Min – Max	Results >LOQ	Min – Max
Aldrin	20	400	1	9.91	1	0.80
cis Chlordane	-	-	0	-	1	21.0
trans Chlordane	-	-	0	-	1	10.6
Dieldrin	10	300	6	<1.25 - 114	3	1.14 – 21.8
Endrin	1	800	0	-	2	2.81 – 9.82
DDD	20	1000	4	14.1 – 913 mean: 249 median: 34.9	2	1.56 – 16.1 mean: 8.83 median: 8.83
DDE	10	1200	16	2.54 – 1020 mean: 100 median: 8.48	16	0.44 – 163 mean: 33.6 median: 8.11
DDT	10	5500	9	3.87 – 560 mean: 107 median: 22.2	10	3.48 – 76.7 mean: 28.0 median: 12.6
Endosulfan (α+β+ sulphate)	-	-	0	-	1	26.4
Heptachlor epoxide	-	-	0	-	1	1.49
Hexachlorobenzene	20	200	4	0.79 - 3.33	4	0.55 – 1.55
Lindane (HCH gamma)	1	8	3	1.38 – 5.28	3	0.84 – 2.43
HCH – alpha	0.3	2	-	-	1	2.57
Methoxychlor	-	-	0	-	1	2.84
Mirex	-	-	0	-	2	2.62 – 24.5

Chlordane, endosulfan, heptachlor epoxide, metoxychlor and mirex were found in one or two samples from agricultural area; and heptachlor epoxide and metoxychlor were found in forest fragment area, but there are not yet established guideline values for these compounds. Endosulfan was allowed for use in soy, coffee, cotton, and sugarcane cultures by mid-2013 in Brazil but was not allowed for tomato culture where it was found.

Comparing the data with a previous study at Alto Tiete watershed (Figure 1), the DDT compounds are the most predominant in both region. Among 108 samples analyzed at Alto Tiete watershed, were found at least one OCP in 31 samples (28.7%), 22 (20.4%) of which from agricultural area and 9 (8.3%) from forest fragments. The

compounds detected were aldrin, dieldrin, DDT/DDE/DDD, lindane and HCB at agricultural area and aldrin, DDT/DDE, lindane and HCB at forest fragment area. The DDT and their isomers was the most abundant and was found in 22 samples (20.4%), 17 of which in agricultural area and 5 in forest fragment area. In nine samples from agricultural area and four samples from forest fragments, were detected one or more OCP in concentration higher than PV, mostly for DDT and their isomers. One sample from agricultural area showed very high levels of DDT and its isomers, reaching levels near the agricultural IV for DDD and DDE, but all other samples results are comparable to the PCJ watershed results levels.

Table2 – Concentrations of OCP quantified in soil samples collected from Forest Fragment area at Alto Tiete watershed (n=60) and Piracicaba/Capivari/Jundiai (PCJ) watershed (n=46)

OCP (□g Kg^{-1} d.w.)	PV	IV agricultural	Alto Tiete		PCJ	
			Results >LOQ	Min – Max	Results >LOQ	Min – Max
Aldrin	20	400	4	2.10 – 10.6	0	-
DDE	10	1200	2	3.20 – 16.2	0	-
DDT	10	5500	3	5.33 – 12.7	0	-
Heptachlor epoxide	-	-	0	-	1	1.94
Hexachlorobenzene	20	200	1	1.76	0	-
Lindane (HCH gamma)	1	8	1	1.38	0	-
Methoxychlor	-	-	0	-	4	2.20 - 8.60

This study did not evaluated the previous cultures to the identified during the soil sampling, therefore the pesticides identified in this study may have been used in the past in other cultures different from the culture identified during the sampling. Most of the pesticides evaluated in this study have been banned many years ago for agricultural use, with exception of endosulfan, and they still remain in agricultural soils.
The presence of some OCPs in some samples from forest fragments may be related to the (1) atmospheric transport and deposition of particulate matter once the forest can be an obstacle for them; (2) surface runoff, once the forest areas studied are small and close from agricultural areas and (3) past use for agriculture.

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