Monitoring of organochlorine pesticides residues in environmental samples and drinking water in Bauru region (SP)

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ABSTRACT

Monitoring of organochlorines pesticides residues was conducted at Bauru (São Paulo) in the period of 1997 to 2002. Elected areas for sampling were based on the agricultural area, soil conducive to agricultural runoff, and location near major aquifers (sugar cane field). The results indicated lower concentration of organochlorine pesticides in finished drinking water, which probably can be related with its adsorption in clay particle presents in supply water or during water treatment process. The results of organochlorine pesticides showed the efficiency of treatment of the distribution net for finished drinking water and water source were compared with the Brazilian classification system for inland waters (CONAMA/86).

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INTRODUCTION

Although pesticides have contributed to a considerable increase in agriculture production their hazardous effects are not neglectable. According to available data hundreds of millions of people, including farmers and consumers, are exposed to dangerous levels of pesticides. Although main users are the USA, western Europe and Japan, almost half the production, in weight, is used by developing countries that, most of the time, use organochlorine pesticide in their cultures, which are more dangerous and have been already banned from more developed countries (EPA, 2000). In Brazil, in the early 80's, the BHC and CCT were extensively used in campaigns against mosquitoes and other insect vectors of diseases such as malaria and Chaga's disease. Their use was limited by the regulation n° 329 of September 2, 1985 and its use was only allowed for control of ants (Aldrin) and in public health campaigns (DDT and BHC).

The problems of intoxication by agriculture defensives is of concern specially due to the fact that intoxication occurs by the gradual ingestion of these products through contaminated water, soil and a variety of foods (CALDAS et al., 2000).

Oganochlorine pesticides are rather inert and its high stability is connected to the carbon-chloride link. There are many studies on this compound due to its high toxicity, low biodegradability and biosolubility in fat tissue (EDWARDS, 1993). Some of these compounds can remain for 15 to 20 years in the soil and part of them can be drawn by rain (by lixiviation) to water flows, which also receive these compounds from industrial discharge and sewerage system, from sediments, from the atmosphere and by direct contamination during its application. Thus, waters from river and dam sources that serve populations and fishes feed with materials from the bottom layer of these places show concentrations of agrotoxics, even years after stopping their use in neighboring regions (SALTZMAN, 1986).

The use of organochorine pesticide in the last decades has produced an accumulation of toxic residues in many ecosystems all over the world. The residues of such pesticides have become an intrinsic part of biological, geological and chemical cycle of the earth and have been detected in water, air, soil, plants, water invertebrates and even in snow and penguins from Antarctica, a place where they have never been used (LUKE et al., 1989).

Regarding the organochlorine compounds analyzed in this study, TABLE 1 shows the index for acute oral toxicity for each

compound and the acceptable daily doses for man (DDA) defined as the doses of the product the can be daily ingested by man without causing health hazard (MINISTÉRIO DA SAÚDE, 2000).

TABLE 1 – Acute oral toxicity (for rats) and Acceptable daily dosis (DDA) of the analyzed organochlorine compounds.

Pesticides	acute oral LD 50 (mg/kg)	maximum DDA (mg/kg)
BHC	(mg/kg)	–
Dieldrin	89	0.0001
Endosulphan	110	–
Aldrin	67	0.0001
Heptachlor	90	0.0005
DDT	250	0.01

The persistence in soil is connected to the sorption forces, dynamic of water flow, solute transport and the degradation rate since when the pesticide reaches the soil there is a partition in three phases of the soil, that is, solid particles, solution and gas (GRUZDYEV, 1983). Water characteristic such as pH, temperature, depth, concentration of suspense floating particles and other dissolved chemical substances imply necessarily in different destiny to pesticides (EDWARDS, 1993).

Usually the conventional treatment technology is not effective in the removal of organochlorine pesticides. Indeed, there are references for almost equal concentrations in plain and treated water (EPA, 1992). In the context of optimization the removal of these pesticides it should be noted the role of activated charcoal, granulated or in powder, as adsorbent. Additionally, such pesticides can also be adsorbed by some types of clay, which, in its turn, are removed by sedimentation/flotation and filtration (MILTNER et al., 1989; PIRBAZARI et al., 2002).

This study presents the evaluation of organochlorine pesticides in samples of plain water, potable water and soil, which were collected in micro-regions with representative cultures of the studied region (Bauru-SP). The study was done from the effluent of a medium size station that treated water in a mean rate of 600 L/s adopting conventional treatment technology without use of activated charcoal.

MATERIAL AND METHODS

SAMPLES:

Analyzes of pesticides in this study refer to the determination of BHC, dieldrin, endosulphan, aldrin, heptachlor and DDT in plain water, treated water and soil. The samples were collected from the summer of 1997 to the summer of 2002. Sample collection was made in three periods: October to December, January to March and April to June. The plain water samples were collect at the bank of rivers and samples of treated water at a distance up to 1 km from the treatment unit. All collections were quintuplicated in order to calculate the precision by the method of relative standard deviation.

REAGENTS:

Alls solvents used were Mallinkrodt (Merck) grade pesticide.

The stock solutions were prepared from certified standard references (purity 98 %, all of them Chem Service Inc.) dissolved in n-hexan and acetone in the concentration of 1 mg/L and the working solutions were obtained from dilutions of the stock solution for the fortified samples.

To concentrate samples it was adopted the solid phase extraction with octadecil (C-18) in 500 mg columns (J.T. Baker).

SAMPLE COLLECTION:

Samples from Batalha and Bauru rivers were collected in average twice a week. All samples were filtered in a 1mm glass fiber filter for removal of particular material and colloids by means of a peristaltic pump.

In each site samples were collected by connecting a 1 L ambar glass recipient to a metal jacket with stem used to aid in the immersion and filling of the recipient. The collection was made immersing the recipient under the water surface (average 1 m deep). After collection the metal jacket was removed and the flask was sealed, cooled in an ice box for transportation to the laboratory. The flasks containing the samples were kept at 4°C until the moment of extraction.

To each period it was assigned a sampling "site of fortification" in which four extra samples were collected in ambar glass flasks, cooled and stored according to the protocol previously mentioned. These samples were fortified by pipetting aliquots of the solution containing the six studied pesticides in three different concentrations: 0.1, 0.5 and 1.0µg/L. Fortified samples and testimony samples were included and extracted in each stage for certification of the integrity of the obtained data.

Potable water

Potable water samples were collected in average twice a week in 1L ambar glass flasks. They were sealed and cooled temporarily with ice for transportation to the laboratory where samples were kept at 4°C until extraction.

Fortification was made using purified Milli-Q water with the studied pesticides in different levels of fortification: 0.1, 0.5 and 1.0µg/L. The obtained samples were submitted to extraction process.

Soil

Soil samples were collected in average twice a week and the collection was done in soils of sugar cane plantation in regions nearby the Batalha and Bauru rivers by digging an orifice of 30cm x 10 cm with an auger and stored in a –18°C freezer until the extraction.

Samples were dried at ~30 ºC. Visible fragments and stones were removed and the samples were then mechanically grinded, sieved at a 60 mesh sieve to attain sample homogeneity and to facilitate the extraction process.

Testimony samples were obtained by extraction of 50g of ground and sieved soil with various solvents as follows: acetonitrile, n-hexane and acetone. The obtained soil sample was dried at 50°C and kept in a desiccator until the extraction. The chromatographic analyzes shows the samples free of organochlorine pesticide residues or any other interfering substance.

The soil testimony samples (circa 10g) were than fortified with 1 mL of the organochlorine pesticides in three levels of concentration: 0.1, 0.5 and 1.0µg/L. The solvent was evaporated to dryness on a flush of nitrogen at room temperature and samples were submitted to extraction process.

EXTRACTION:

Water samples

The concentration and purification of water samples were made by Solid Phase Extraction (SFE) with SPE-C-18 cartridges as adsorbent and a Supelco Visiprep vacuum system. Five water samples were extracted adding 1,000 mL of water to the cartridges and eluding them with 5 mL of ethil acetate and 5 mL of dichlormethane (on vacuum). The final aliquots were combined (10 mL of eluent), concentrated by N_2 flux to dryness and the volume was adjusted with 1mL of n-hexane, followed by gas chromatographic analyzes (HRGS/ECD).

The procedures for preparation and extraction have enhanced in 100 folds the concentration of the analite.

Soil samples

A 10g soil sample (after drying, grinding and sieving) was extracted with 100mL of n-hexane under constant stirring during 30 minutes. Then, the suspension was centrifugate for 20 minutes and the liquid layer was filtered in a glass membrane filter (0.22 µm) with repetition of the stirring and filtration steps.

The combined extracts were concentrated to dryness in a rotaevaporator on vacuum at 45°C. The residue was solubilized in 1mL of n-hexane for analyzes by HRGC/ECD. The fortification process were done in quintuplicate for each level together with one testimony being extracted and analyzed for precision evaluation (relative standard deviation) as well as for possible interferences from the analytical process.

Analyzes

The obtained extracts were then submitted to HRGC analyzes in a gas chromatograph HP 5890 series II equipped with a electron capture detector (ECD-^{63}Ni) at 300°C using H_2 as dragging gas ($\bar{\mu}$= 38 cm/s) and make up flux of N_2 66 mL/min. The used column was a LM-5 (5% phenildimethilpolisiloxano) with 30mm x 0.25mm with a film 0.35 mm thick. The oven temperature was 80°C (12 min) to 300°C (5 min.) at 8°C/min. All samples were injected in split mode (1:25) at 250°C.

RESULT

In TABLE 2 it can be seen the maximum allowed concentration of organochlorine pesticides evaluated for human use water (MINISTÉRIO DA SAÚDE, 2000) and of fresh water for public use (CONAMA, 1986). Results of the analyses can be seen in FIGURES 1 and 2.

TABLE 2 – Maximum concentration of the evaluated pesticides according to Conama and the allowed values (AV) for the evaluated pesticides for drinking water.

Pesticides (µg/L)	AV (µg/L)	Class 2	Class 3
BHC	2.00	0.02	3.00
Dieldrin	0.03	0.005	0.03
Endosulphan	20.00	0.056	150.00
Aldrin	0.03	0.01	0.03
Heptachlor	0.03	0.01	0.10
DDT	2.00	0.002	1.00

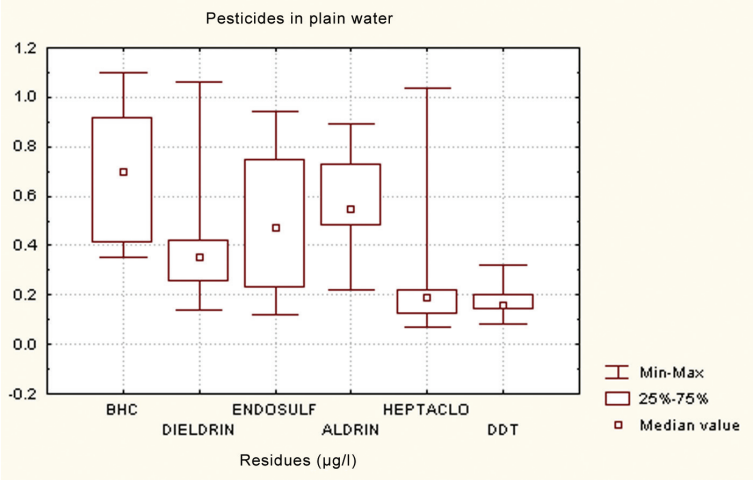

FIGURE 1 – Median and distribution of the concentration of organochlorine pesticides in plain water during the studied period.

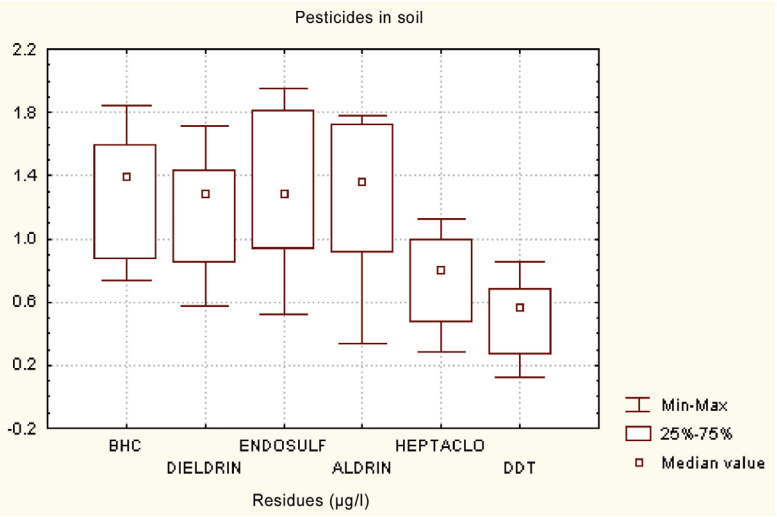

FIGURE 2 – Median and distribution of the concentration of organochlorine pesticides in soil during the studied period.

DISCUSSION

In FIGURE 1 it's observed that the contents of pesticide in plain water were always above the limits of Class 2 and, most of the time, superior to the limits for Class 3. It's important to stress that Diledrin and Aldrin, considered as highly toxic, and the heptachlor showed concentration superior to those established by the Conama (CONAMA, 1986) for Class 3 water flows in 100% and 80% of the analyzes, respectively (TABLE 2). In this connection, the impound water from this specific river, in thesis, could not be used to public

distribution. The same applies for the turbidity of plain water, which maximum limits (100 μT for Class 3) is surpassed in most distribution system in the country.

In what regards the treated water, out of 90 analyzes on 6 studied organochlorine pesticides, in 10 situations there was a concentration superior to those established by the Regulation n° 1469. Such results regards to the same pesticides mentioned, which concentration in plain water surpass the limits established by the Conoma and presented the lowest Maximum Allowed Values for drinking water (TABLE 1). It is important to note that Aldrin and Dieldrin showed 8 results above the potability standards – five out of which, in the last sampled period between October 2000 and June 2002. However, there was a weak correlation between the concentration of these pesticides in plain water and the parent treated water, which rates were 0.62 and 0.47 respectively.

As can be seen in TABLE 3 the values for the rates of correlation between plain water and soil are low, which indicates greater concentration of pesticides in soil. The soil contamination is influenced by the molecular structure of the pesticide, its concentration in the soil, temperature, humidity and physical and chemical characteristics of the soil.

The solid particles of organic mineral material (clay, silt, sand and organic material) are important in the process soil adsorption of pesticide. The clay soil shows a greater rate of adsorption. This effect is less pronounced in Bauru since its soil shows a mix characteristic with a tendency to quartzozo soil type what justify the concentrations of pesticides found also in plain water.

TABLE 3 – Correlation rate between the concentration of pesticides in plain and treated water and plain water and soil.

Pesticides	Rate for plain water x soil	Rate for plain x treated water
BHC	0.63	0.68
Dieldrin	0.56	0.58
Endosulphan	0.65	0.15
Aldrin	0.84	0.51
Heptachlor	0.48	0.52

CONCLUSION

As the treatment station does not have or does not use any kind of product specific for organochlorine pesticide removal, the results of the analyzes of treated water, together with the volatility of some pesticides, are probably due to the high adsorption potential of the clay present in the drainage basin, even though selective. In this context, one can expeculate, the adsorption of Aldrin by clay particles seems to be less significant facing the greater correlation rate (0.84) for plain and treated waters, as verified for the evaluated pesticides. Probably, the greater increase of this pesticide would become noticeable in the deterioration of the quality of the water used by the population, worsened by the low concentration established by the Standard of Potability (0.03mg/L). In any case, it was identified the importance of the knowledge of the turbidity in the different phases of the system, considering that this parameter is essential to the evaluation of the efficiency of the treatment unit in the prospective of the removal of protozoa and enterovirus as it is for the removal of pesticides.

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