Removal of Pesticides in Water of Rio de la Plata (*In Vitro* Assay)

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INTRODUCTION

Environment pollution by organic pesticides is,at present,a subject of preoccupation.It is so,because of their great toxicity and persistance,and because of their great consume,with the aggravating that some of them offer metabolites even more toxic than their respective precursors.

Is is worthless to discuss the invaluable contribution of pesticides to the increase of agricultural productivity,but every effort tending to decrease the side effects due to their permanence in the environment will be insufficient,as in many cases the view of unbalanced conditions in the natural environment is insuperable.

Fauna and flora related to aquatic environment may be overtaken by pesticides.So far beginning the present work,data on contamination by pesticides in Rio de La Plata were lacking,thus arising the need to conduct stu dies in this respect.It has been done in a coastal section which is characteristic by frequent leakages of petroleum and the presence of industries releasing waste waters there;the region also receives the tribute of effluents coming from zones destined to horticulture and floriculture,where the use of pesticides is intensive.

No pesticides or their metabolites have been detected in waters from the region under study;that lack has been adscribed to factors such as codistillation,chemi-

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cal degradation,microbiological degradation,photodescomposition,biological magnification and adsorption by the solid suspended matter,which contribute to water autodepuration,concerning pesticides (BOWMAN et al 1964; HILL & McCARTY 1967; HUANG 1971).

This induced to employ four pesticides currently used,to study in vitro,the influence of codistillation and descomposition,and also of adsorption.

MATERIALS AND METHODS

Samples of superficial water were taken at three sites of a coastal section its length 10 Km,at a distance from the coast ranging between 50 and 100 metres Aliquots were taken from the total volume to perform the assays.

The pesticides tested were: Heptachlor,Malathion, Endrin and DDT.They were extracted employing petroleum ether(pesticide grade) and anhydrous sodium sulfate p.a. Glass apparatus with teflon stopcocks and ground joints were used for extraction and concentration.

The analysis was carried out in a Fractovap GT Carlo Erba chromatograph equipped with an electron capture detector (source of Ni-63).

The columns used were 2 m x 6 mm o.d. glass tubes fitted with 1 % SE-30 on Gas Chromosorb P silanized (100-120 mesh).The oven temperature was set at 170 C, the injector at 190 C,and the detector at 250 C.The flow rate of the purified nitrogen carrier was 50 ml'm.

Blank assays on samples of water and suspention materials were performed in order to know the possible presence of pesticides in those fractions.

To determine the removal due to codistillation and the other factors above mentioned,known amounts of Heptachlor,Malathion,Endrin and DDT were incubated in natural and filtered water.Were made the following assays:

a) Blank of water: 500 ml river filtered water through membrane filter pore size 0.2 microns.
b) Blank of suspension materials: 500 ml river water were centrifuged at 10,000 x g for 20 minutes in a Sorvall centrifuge.Supernatant was discarded.
c) Suspension matter-free water: 5 litres filtered river water as already described,were poured into a 9 litres glass container.
d) Natural water: 5 litres of river water poured into a glass container the same shape and size as the forementioned.

0,5 mg (0.1 p.p.m.) of each pesticide,dissolved in acetone,was added to the containers c) and d).They were kept at room temperature,11-15 C,for 72 hours with an air bubbling of 400 ml'minute.

At times 0 hs.(immediately after adding pesticide acetonic solution),24 hrs,48 hrs and 72 hrs,500 ml-samples of water were taken from both containers.The aliquots from container d) were centrifuged at 10,000 x g for 20 minutes,and the sediment separated.

Pesticides were extracted from water samples according to MESTRES et al (1969). -Portions of 10 ml,5 ml and 5 ml of petroleum ether were used to extract them from sediments by shaking for 10 minutes in separatory funnels.The extracts being dried with anhydrous sodium sulfate,were conveniently concentrated in Kuderna-Danish evaporators and analyzed by gas-liquid chromatography.

The supernatants from centrifugations at 10,000 g for 20 minutes and the filtrates through membranes,were both considered free from microorganisms and inert matter except colloidal clay.By centrifuging the 10,000 g supernatant for 20 minutes at 30,000 g for 20 minutes in a Spinco centrifuge,and observing no sediment,it was corroborated that centrifugation under those conditions achieves the same results as the filtration through membranes.

RESULTS AND DISCUSSION

Ether extracts analyses of the "blank" of water and suspension matter did not reveal the presence of any pesticide;they were carried out with a sensitiveness that would have allowed to detect amounts on that order of 0.0002 p.p.m.

In suspension matter-free water (filtered river water),a greater removal of DDT and Heptachlor than that of Endrin and Malathion is observed (Table 1). Similar differences,though less notorious,could be observed during incubation performed with natural water (Table 2)

TABLE 1

% of pesticides that remains in the medium (suspension matter-free water)

Time	0 hrs.	24 hrs.	48 hrs.	72 hrs.
Heptachlor	100	83.5	68.4	55.4
Malathion	100	108.5	102.0	109.0
Endrin	100	95.9	95.4	89.8
DDT	100	80.1	69.1	62.7

The removal might attributed namely to codistillation with water,since from the parameters responsible for that action,in working conditions,it is the fundamental.That has been proved in the experience done with filtered water;that is the main parameter to be taken into account,since chemical descomposition in aqueous medium would only be reached in the presence of high oxi-

dant concentrations or strong alcaline medio absent in the assay conditions and in natural medium. (BUESCHER et.al, 1964; LEIGH 1969).

TABLE 2

% of pesticides that remains in the medium (natural water)

Time	0 hrs.	24 hrs.	48 hrs.	72 hrs.
Heptachlor	100	85.5	82.5	67.2
Malathion	100	100.7	106.5	94.3
Endrin	100	96.4	104.0	91.3
DDT	100	81.7	78.0	74.0

TABLE 3

% of pesticides that remains in the medium (sediment)

Time	0 hrs.	24 hrs.	48 hrs.	72 hrs.
Heptachlor	76.0	100	89.9	82.9
Malathion	--	--	--	--
Endrin	65.9	100	81.7	74.7
DDT	46.6	100	87.8	68.0

The possible removal of these pesticides by microbian metabolization in the natural water (assay d) was discarded, as no chromatographic peaks corresponding to their common metabolites were found.

The three chlorinated pesticides tested are immediately adsorbed by the matter in suspension. Table 3 presents the results; the progressive removal that is observed starting at 24 hours, may be due to desorption and perhaps

to a descomposition.This is important for the incidence it may have on the feeding of filtering fish which in the zone are destined to human consume,and which surely are part of a trophic chain.

Not any presence of Malathion was noted in the sediment obtained by centrifugation of natural water (assay d).The conception that removal from water may be principally due to codistillation with it,is reenforced by the fact that Malathion,which does not disappear being itself of a low solubility,is precisely among those employed,the one of a higher solubility in water.

No significants differences were observed when the assays were made in autumn and in spring.The results showed in the tables are the average of two determinations carried out in both seasons.

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