INTERACTION BETWEEN PESTICIDES AND HUMIC SUBSTANCES FROM TROPICAL COASTAL LAGOONS[1]

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In the northwest coastal plain of Mexico there are several coastal lagoons (375,000 ha) of great ecologic and economic importance and also the most important and technified agricultural fields (1,500,000 ha irrigated fields) of the country. In these fields very large amounts of pesticides are applied each year and their residues enter the lagoons mainly by the agricultural drainage [3].

Those lagoons are surrounded by mangroves which are an important source of humic substances (HS), the HS reach concentrations of 100 mg/L during the rainy season [1] and can interact with pesticide residues affecting, among others, the solubility, sorption, bioaccumulation and bioavailability of the pesticides through the formation of complex molecules [2]. As with other type of contaminants the study of the interactions between pesticides and HS is of great importance for the appropriate management of coastal areas impacted by agricultural runoff.

The HS that enter the lagoons with freshwater runoff tend to precipitate with salinity. Experiments were done in laboratory to determine the effect of HS (isolated from coastal lagoons) and humic acids (HA) (Aldrich) on the partition of selected pesticides between water and sediment phases. Due to the accurate results obtained with radio-labelled compounds, ^{14}C-labelled pesticides were used for the experiments. The selected pesticides were: chlorpyrifos (o,o-di-[1-^{14}C]ethyl o-3,5,6-trichloro-2-pyridil phosphorotioate), DDT (1,1,1-trichloro-2,2-bis(p-chloro-[ring-U-^{14}C]-phenyl)ethane) and parathion (o,o-diethyl o-4-nitro-[ring-U-^{14}C]-phenyl phosphorotioate).

The ^{14}C-labelled pesticides were spiked in separate glass jars with sea water (38 o/oo) and then, in different experiments, aliquots of a distilled water stock solution of HS and HA were added. After one hour at room temperature the jars were centrifuged to separate water and the pellets of precipitated humics. Absorbance (380 nm) of the supernatants was recorded to evaluate the percentage of precipitated humics. The HS and HA pellets were extracted with hexane in a sonic bath and centrifuged again. The ^{14}C radioactivity (dpm) of the pellets, of the hexane fraction and of the aqueous fraction were measured with liquid scintillation counter (Packard 2100TR) to determine the amounts of ^{14}C-pesticides bonded to the precipitated humics.

The results obtained indicate that from 70 to 90% of the HS and HA that enter into sea water precipitate, with 10 to 30% of them remaining in solution. After gel filtration chromatography (Sephadex G-15) of aliquots of HS and HA stock solutions, it seems that the precipitated humics are high molecular compounds and the soluble humics are low molecular weight compounds (~200 Daltons).

The percentage of activity measured in the pellets (Figs. 1-2) indicate that a significant percentage of DDT is strongly bond to the humics precipitate (76% for HA and 36% for HS), probably due to its low water solubility. For chlorpyrifos, that has also a low solubility in water, there is an important percentage of compound bonded to the humics that precipitate (32% for HA and 13% for HS) and for parathion, that has a high solubility in water, there was a small amount of pesticide bonded to the humics precipitate (8% for both HA and HS).

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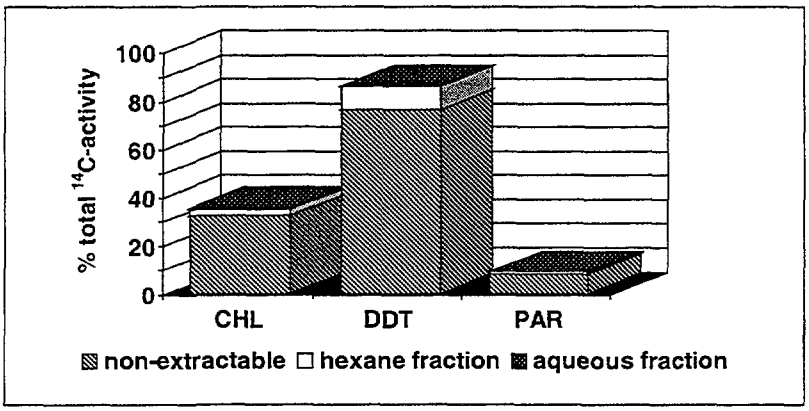

FIG. 1. Percentage of total activity of ^{14}C-labelled pesticides in humic acids pellet. CHL = chlorpyrifos; PAR=parathion.

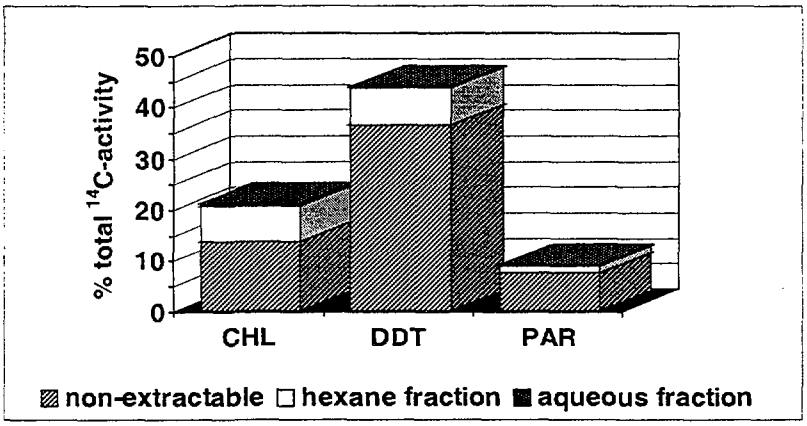

FIG. 2. Percentage of total activity of ^{14}C-labelled pesticides in lagoon humic substances pellet. CHL = chlorpyrifos; PAR=parathion.

With the results obtained we concluded that significant percentages of certain pesticides that enter coastal lagoons, with brackish or marine conditions, can form complex compounds with HS which precipitate. Evidently the pesticides-HS complexes will have different dynamics in the environment (sorption, degradation, partition, bioavailability, etc.) than pesticides alone.

The presence of HS in coastal waters seems to prevent, to a certain extent, pesticide pollution through elimination of pesticides by sequestering them in the sedimentary phase. Preliminary results of mussels (*Mytillus galoprovincialis*) exposed to ^{14}C-labelled pesticides in the presence and absence of HS, indicate that uptake of pesticides by the organisms is less in the presence of HS (González-Farias *et al.*, in prep.). With these results its evident that HS tend to diminish the impact of pesticides over aquatic ecosystems and confirms the results of other authors [4].

References

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