ORGANOCHLORINE PESTICIDES IN SEDIMENT AND BIOLOGICAL SAMPLES FROM THE COASTAL LAGOONS OF NICARAGUA

S. MONTENEGRO, M. LACAYO, F. PICADO, A. LOPEZ
Aquatic Resources Research Center,
National Autonomous University of Nicaragua,
Managua, Nicaragua

Abstract

A study was carried out on the Pacific coast of Nicaragua to investigate the contamination of the coastal lagoons with residues of agricultural pesticides. Samples were taken during 1995 from the areas of Estero Real, Padre Ramos, Maderas Negras, Naranjo and Paso Caballos, and during 1996 from Aposentillo to Estero Barquito - Posoltega River. Analysis of the samples of sediment and aquatic life (fishes, oysters and bivalves) showed that they were contaminated with organochlorine pesticides. The pesticides found in the highest concentrations were toxaphene (1,734 $\mu g.kg^{-1}$) and p,p-DDE (275 $\mu g\ kg^{-1}$). These data indicate widespread contamination of the ecosystem with organochlorine pesticides in the main Pacific coastal lagoons of Nicaragua, resulting from intensive agricultural use of pesticides during the past decades. The contamination has been carried from the agricultural areas to the coastal lagoons by the rivers passing through the cultivated areas.

1. INTRODUCTION

The districts of Leon and Chinandega, located in the west coast of Nicaragua, have the highest agricultural activity in the country due to fertile soil of volcanic origin and favourable climatic conditions which help in growing a wide variety of crops. Also the main underground water supplies for the pacific coast are found in this region. Nevertheless, intensive farming for the last 40 years has caused damage to the soil, and the water has been contaminated due to generalization of single crop farming (cotton and sugar cane) . The soils superficial layer has been deprived of nutrients by single crop farming. The excessive use of pesticides has degraded and accelerated the contamination of soil and water.

Very little information is available regarding the contamination of coastal lagoons or estuaries with by pesticide residues in Nicaragua. Most of the estuaries, covered by vast mangrove forests, collect the drainage from the agricultural fields. The mangroves create an interface of sea and land area, and receive water from tides as well as the streams and surface run off from the land. Thus there is a continuous turn over of the soil and nutrients and organic matter, with an overall los from the land to the coastal water. In the the estuaries the rivers discharge silt, creating a platform of mud where the organic matter accumulates.

Atoya river is the main river that flows through Chinandega, and has a basin of 354 square kilometers. This river discharges within the system of coastal lagoons, which has an area of 155 square kilometers, and it is surrounded by a vast mangrove. Marine resources are exploited, and they represent a considerable fraction of the local populations diet. Therefore, contamination of these resources with pesticide residues would represent a potential health risk to the consumers sea food and fish from the lagoons. The aim of this study was to investigate the distribution, fate and effects of organochlorine pesticides in sediments, fish and bivalves tissues of the coastal lagoons system.

2. METHODS AND MATERIALS

Samples were obtained from the Pacific coast (Fig 1) during two field trips. In the December 1995 field trip sediment samples were collected from the following locations: Estero Real, Estero Padre Ramos, Estero Maderas Negras-Paso Caballos. In the September 1996 samples of sediments, fish, oysters and Anadara spp were collected from Estero Aserradores, Estero El Realejo, Estero Grande, Estero El Barquito, and the Atoya river.

2.1. Sampling of sediment

The superficial sediment samples were collected with the Eckman grabber, homogenized and transfered into previously washed glass jars labelled with precise information on the sampling sites. The collection of sediment at different depths was carried out with a soil core sampler.

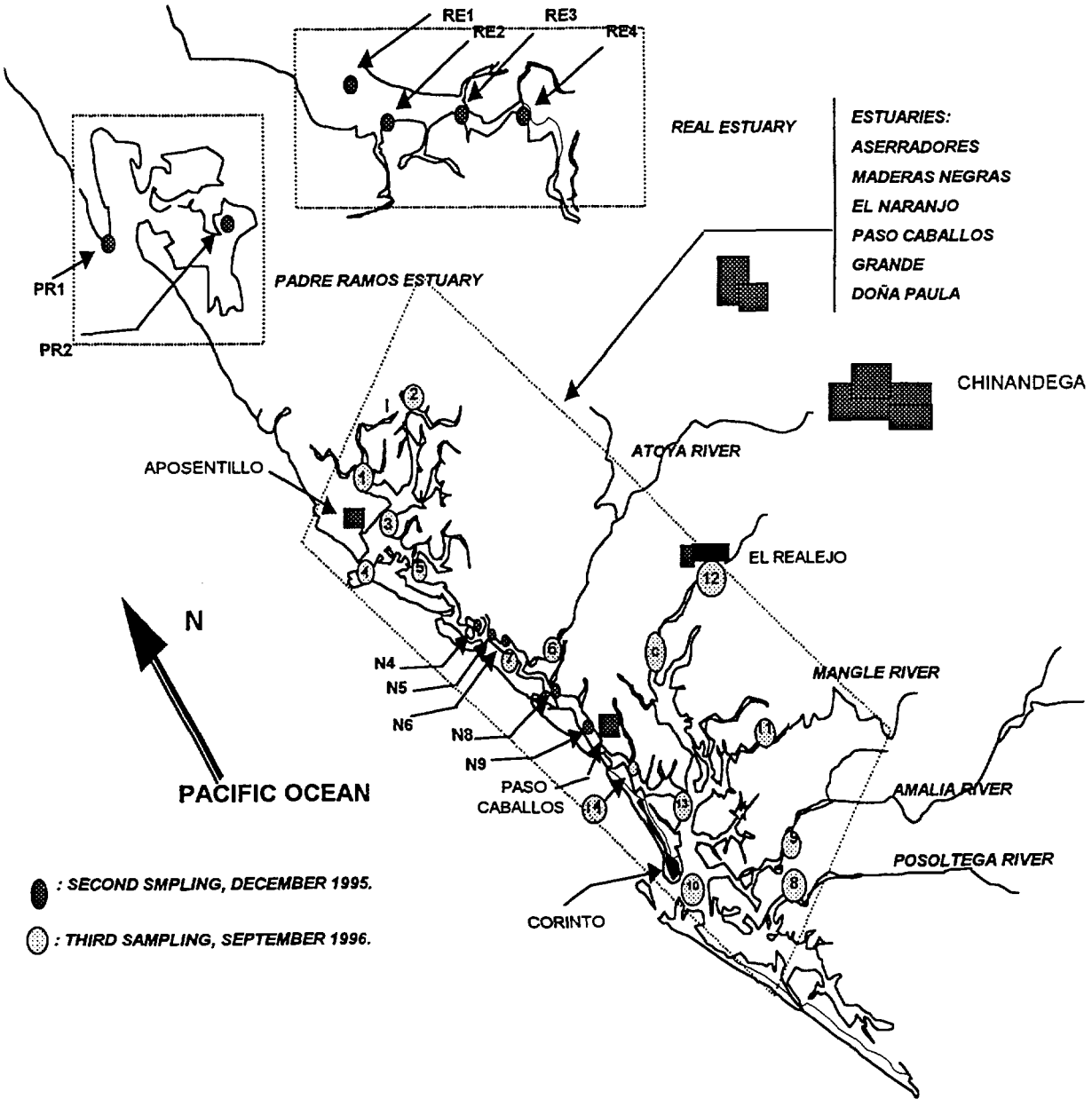

Fig. 1. Map of sampling points along the coast of Nicaragua

All sediment samples were kept cold during transport to the laboratory. The sediment cores were cut into 5 cm sections, weighed, and dried at room temperature. Sections of the same depth were pooled to obtain samples of the minimum weight requirement for the analysis of organochlorine pesticides [1].

2.2. Sampling of biological tissues

Fish and clam samples were collected with the aid of local fishermen in the following sites: Monte Redondo (Atoya River), Alemania Federal, El Realejo, La Lapa Estuary and Paso Caballo. The samples were transported to the Marine Environment Laboratory (MEL) in Monaco of International Atomic Energy Agency (IAEA), then dry-frozen to be sent to CIRA laboratory for the analysis of pesticides residues. Ten grams (dry weight)of tissue sample were used for extraction and residue analysis.

2.3. Analytical quality control

In order to ensure the precision of the analysis, known concentrations of pesticide standards were spiked in each group of sediment and biological tissue samples to be extracted. The percent of recovery of each spiked pesticide was calculated to test the performance of the analytical method used in this study.

Duplicate analysis for each group of sediment samples and biological tissues samples, were carried out to control the reproducibility of the analysis. A target, a fortified sample with known concentrations of organochlorine pesticides, and a fortified sample of toxaphene, were included in each group. An internal standard was added to all samples from the start of the analysis to assure that all organochlorine pesticides were detected. When the percentage of recovery for HCB was less than 70 %, the samples were analyzed again. The mean percentage of recovery for HCB in sediment samples was 74 %, and for biological tissues was 76 %. Another analytical quality control exercise in this work was the interlaboratory analysis of identical samples. This was carried out by the laboratories of CIRA/UNAN and the MEL, Monaco to compare the reproducibility of the analytical results.

2.4. Analytical procedures

The pesticides from the sediment or tissue samples were extracted with a mixture of hexane + methylene chloride, and the concentrated extract was analysed with a model 3400 Varian gas chromatograph(GC). The GC was equipped with an electron capture detector (ECD) and a DB5 capillary column with a length of 30 meters, and an internal diameter of 0.32 mm.

A micro liter of sample was injected, in the splitless mode. Hydrogen was used as a carrier gas and Nitrogen as the make up gas. The temperature program used for the analysis was the following : 80 ^{0}C (1 minute), 4 ^{0}C/min. to 200 ^{0}C, 3 ^{0}C/min. to 230 °C, 15 °C /min. to 250 °C (5 minutes) . The temperatures for the detector and the injector were 350 °C and 250 °C respectively. The peaks were identified comparing retention times with those for the best quality analytical standards, (Supelco Inc.) . The concentrations of the residues from pesticides were calculated on the basis of a calibration curve, using an internal standard.

3. RESULTS

3.1. Pesticide residues in sediment

In the samples taken during the second field trip during December 1995 fifteen organochlorine pesticides were targeted for analysis in the superficial and stratified sediment. The pesticides with

high concentrations were: toxaphene, p,p-DDE, p,p-DDD, lindane, dieldrin, and p,p-DDT. Endrin, α-endosulfan and heptachlor, were detected in lower concentrations. Aldrin, α-BHC, β-BHC, δ-BHC, β-ndosulfan and heptachlor epoxide were not detected in any of the samples analyzed.

Table 1 shows concentrations of organochlorine pesticides found in the superficial sediment samples taken during 1995. p,p-DDE was found in superficial sediment samples from all sampling sites, except sampling site PR1. The concentration of pp-DDE ranged from 0.87 to 130.34 $\mu g.kg^{-1}$. p,p-DDD was detected at sampling sites N4, N5 and N6, at a concentration ranging from 7.18 to 28.79 $\mu g.kg^{-1}$. Dieldrin was found at all sampling stations, except stations N5 and PR2, with concentrations ranging from 0.59 to 53.73 $\mu g.kg^{-1}$. Residues from p,p-DDT were detected at sampling stations N4, N5, N6 and N9, and the concentrations ranged from 1.63 to 32.22 $\mu g.kg^{-1}$. Endrin was found at stations N4 and N6 with concentrations of 1.97 and 2.90 $\mu g.kg^{-1}$ respectively. Heptachlor was detected at stations N4, N8, ER1, ER2 and ER3, with concentrations ranging from 0.56 to 0.76 $\mu g.kg^{-1}$ Toxaphene was detected only at station N4, with a concentration of 468.43 $\mu g.kg^{-1}$. This high concentration is probably due to the proximity to a town where cotton was cultivated. The detection of p,p-DDE at all sampling stations, except station PR1, is probably due to the wide spread use of the pesticide p,p-DDT in this area for a variety of crops, mainly cotton.

Sampling station N4 showed the highest degree of contamination with residues of organochlorine pesticides. Seven of the 15 pesticides targeted for analysis were found at this station, and this is most likely due to the proximity of the sampling site to the town of San Miguel where cotton was cultivated. All other sampling stations are located farther away from towns.

Table 2 shows concentrations of pesticides found in the stratified sediment core samples taken during 1995. The samples were taken at five increasing depths of 5 cm down to 25 cm and represent four sampling sites N4 (Naranjo 1), N5 (Naranjo 2), N8 (Santa Ana 1) and N9 (Paso Caballos). The results showed presence of p,p-DDE (18.53 to 274.64 $\mu g.kg^{-1}$), p,p-DDT (1.75 to 48.74 $\mu g.kg^{-1}$) and p,p-DDD was detected with a maximum concentration of 89.07 $\mu g.kg^{-1}$.

Endrin was detected at three sampling sites. The maximum concentration was 6.49 $mg.kg^{-1}$ at 5-10 cm at sampling site N4. This compound was not detected at the sampling site N8. Dieldrin was detected at all depths down to 25 cm at sampling sites N4 and N5, and the concentration ranged from 0.69 $\mu g.kg^{-1}$ to 17.29 $\mu g.kg^{-1}$. However, at sampling site N8 it was found only in the upper 5 cm layer, and at the sampling site N9 it was not detected at all. Heptachlor was present at sampling sites N4, N8 and N9. At N4 it was detected only in the upper 0-5 cm section of the stratified sediment. At N8 it was detected at all superficial and stratified sediments except at the 5-10 cm depth . Lindane was found in the sediments collected at a depth of 5-10 cm at N4. At N9 lindane was detected at the 10-15cm, 15-20 cm, and 20-25 cm in superficial and stratified sediments.

Residues of α-Endosulfan were present in a few samples of the sediment. These included the upper 10 cm sediment at sampling site N4, 15-20 cm section at N5, and 20-25 cm and sampling site N9. Toxaphene was found at two sampling sites: N4 and N5, but at all depth sampled at both sites.

Table 3 shows data on the residues of organochlorine pesticides found in surface sediment samples taken during 1996 from 14 sampling sites. Aldrin, heptachlor and lindane were detected at

TABLE 1. RESIDUES OF ORGANOCHLORINE PESTICIDES IN SURFACE SEDIMENT SAMPLES TAKEN AT SAMPLING SITES DURING 1995

Sampling sites	Organoclorine pesticides detected ($\mu g. kg^{-1}$). Heptachlor	Endrin	Dieldrin	p,p- DDT	p,p- DDE	p,p- DDD	Toxaphene
N4 (Naranjo 1)	0.68	1.97	2.33	32.22	130.34	28.79	468.43
N5 (Naranjo 2)	ND	ND	ND	10.46	38.64	13.81	ND
N6 (Naranjo 3)	ND	2.90	1.50	8.63	17.34	7.18	ND
N8 (Sta.Ana)	0.55	ND	1.29	ND	0.87	ND	ND
N9 (P.Caball.)	ND	ND	53.73	1.63	9.92	ND	ND
RE1	0.76	ND	30.33	ND	3.42	ND	ND
RE2	0.98	ND	1.38	ND	2.38	ND	ND
RE3	0.66	ND	4.23	ND	1.95	ND	ND
RE4	ND	ND	1.04	ND	5.77	ND	ND
PR1	ND	ND	0.59	ND	ND	ND	ND
PR2	ND	ND	ND	ND	2.19	ND	ND

ND: No detected

TABLE 2. RESIDUES OF ORGANOCHLORINE PESTICIDES IN STRATIFIED SEDIMENT SAMPLES TAKEN DURING 1995

Sampling sites		Organochlorine Pesticides detected µg. kg^{-1}								
		Heptach.	Lindane	a-Endosul.	Endrin	Dieldrin	p,p- DDT	p,p- DDE	p,p- DDD	Toxaphene
Naranjo 1" (N4)	0 -5	0.64	ND	1.7	2.32	7.99	38.07	107.59	38.72	553.61
	5-10	ND	1.24	2.81	6.49	8.65	45.80	127.84	48.93	740.66
	10-15	ND	ND	ND	4.94	5.86	40.59	192.36	45.06	1733.93
	15-20	ND	ND	ND	2.69	3.00	44.57	241.26	42.83	1216.15
	20-25	ND	ND	ND	2.04	1.98	19.92	127.73	19.91	457.89
Naranjo 2' (N5)	0-5	ND	ND	ND	3.02	9.22	36.49	257.73	52.28	1116.85
	5-10	ND	ND	ND	3.90	17.29	37.32	204.53	36.22	793.40
	10-15	ND	ND	ND	3.15	12.64	35.57	164.99	28.87	691.60
	15-20	ND	ND	2.30	1.73	6.06	45.37	128.33	29.62	646.70
	20-25	ND	ND	ND	2.30	11.51	48.74	274.64	89.07	487.63
Sta ANA 1' (N8)	0-5	0.43	ND	ND	ND	0.69	3.38	18.53	3.52	ND
	5-10	ND	ND	ND	ND	ND	1.75	26.25	4.45	ND
	10-15	0.32	ND	ND	ND	ND	2.48	30.97	4.76	ND
	15-20	0.20	ND	ND	ND	ND	2.54	61.09	11.55	ND
	20-25	0.09	ND	ND	ND	ND	2.79	39.89	4.79	ND
P.CABALLO 2 (N9)	0-5	0.07	ND	ND	ND	ND	4.32	74.63	9.62	ND
	5-10	ND	ND	ND	ND	ND	2.57	51.95	6.37	ND
	10-15	ND	23.86	ND	1.27	ND	2.34	49.80	10.23	ND
	15-20	0.15	2.15	ND	ND	ND	5.56	184.66	41.99	ND
	20-25	ND	71.29	1.89	3.75	ND	3.41	86.38	30.09	ND

TABLE 3. RESIDUES OF RGANOCHLORINE PESTICIDES DETECTED IN SURFACE SEDIMENT SAMPLES TAKEN DURING 1996

Sampling sites	Organochlorine pesticides detected (µg. kg $^{-1}$) Heptachlor	Lindane	Aldrin	Endrin	Dieldrin	pp'-DDT	pp'-DDE	pp'-DDD	Toxaphene
STATION 1	ND	ND	ND	ND	ND	2.05	31.17	3.21	ND
STATION 2	ND	ND	ND	ND	ND	ND	2.71	ND	ND
STATION 3	ND	ND	ND	ND	ND	1.26	18.02	2.18	ND
STATION 5	ND	ND	ND	ND	ND	0.95	16.47	2.24	ND
STATION 6	0.90	0.48	1.19	3.05	10.23	49.62	58.97	46.05	1,309.41
STATION 8	ND	ND	ND	1.01	8.30	35.77	58.73	26.23	589.44
STATION 9	ND	ND	ND	0.62	5.10	7.08	43.74	11.35	220.81
STATION 10	ND	ND	ND	ND	4.50	0.78	7.74	1.06	ND
STATION 11	ND	ND	ND	ND	4.19	8.45	59.21	9.73	184.45
STATION 12	ND	ND	ND	1.40	8.03	29.96	93.99	21.11	348.15
STATION 13	ND	ND	ND	ND	3.75	10.95	52.92	10.93	ND
STATION 14	ND	ND	ND	ND	8.39	3.06	20.57	4.73	ND

three sites only, and 6 of the other targeted pesticides were detected from more sites. The DDT group of compouds were detected with the greatest frequency. At sampling site 2 only DDE was detected. Absence of detectable quantities of the other pesticides from this site may be due to a low degree of farming in this area in the past. More pesticides have been detected at the other sampling sites, and this may be because the river water flowing through lands cultivated with cotton and sugarcane for decades and contaminated with pesticide residues would be expected to spread the contamination into these sampling sites.

Sampling sites 6, 8, 9, 11, 12 and 13 contained higher concentrations of p,p-DDE, p,p-DDD and p,p-DDT than the other sites, with maximum concentration of 93.99, 46.05 and 49.62 $\mu g.kg^{-1}$,respectively. The highest concentration of p,p-DDE was found at the sampling site 12, which is caracterized as a poor mangrove forest located near the town of Realejo and where sugar cane and cotton crops were cultivated. These compounds are resistant to breakdown and are readily adsorbed into sediments and soils, which can act both as sinks and as long-term sources of exposure for soil organisms [2]. The highest concentrations of p,p-DDD and p,p-DDT were found at site 6, and this may be due to the influence of the Atoya River and its tributaries (Sasama and Acome). Albone et al. [3] investigated the capacity of river sediments, from the Severn Estuary, United Kingdom, to degrade DDT. p,p'-DDT (^{14}C labelled) was applied to sediments either in situ on the mud flats or in the laboratory. Incubation in situ over 46 days led to very little metabolism of DDT in the sediments. Some p,p'-TDE was produced, but the ratio of DDT to TDE was 13:1 and 48:1 in two replicate experiments. Incubation of the same sediments in the laboratory, over 21 days, led to much greater metabolism (ratios of 1 : 1.1 and 1 : 3.3, DDT to TDE in replicate incubatios) and the production of some unidentified, further breakdown products.

Dieldrin was detected at sites 6-14. It was not detected at sites 1-5, probably due to the location of these sites where very little agricultural cultivation has been practiced in the past or possibly due to little use of dieldrin at these sites in past. The concentration of dieldrin at sites 6-14 ranged from 3.75 to 10.52 $\mu g.kg^{-1}$. Higher concentrations were found at the sampling sites 6, 8, 12 and 14, with the highest at site 6. This can be attributed to the intensive production of crops such as cotton, sugar cane in the past, and banana, sorghum, sesame seed, peanut and other crops at the present time.

Detectable residues of endrin were found only at sampling sites 6, 8, 9 and 12 in concentrations ranging between 0.62 and 30.55 $\mu g.kg^{-1}$. Lower residues indicate that this pesticide had been used in this area on a smaller scale.

Toxaphene was detected at the highest concentration of any pesticide during the 1996 sediment sampling campaign. It was detected at a concentration of 1309.41 $\mu g.kg^{-1}$ in sediment at site 6, which is located at the Atoya River. This indicates that toxaphene has been used widely in the past and may still be illegally in use, its use was banned during 1980. Another site with high concentration of toxaphene (589.44 $\mu g.kg^{-1}$) was site 8, which is situated at the Posoltega River. Intensive cotton cultivation was practiced in this area. Toxaphene was also found at sites 9, 11 and 12 but in low concentrations.

Table 4 shows concentrations of pesticides found in 5 cm sections of the stratified sediment core samples taken during 1996 at the sampling site Puerto Realejo. The detected pesticides included p,p-DDE, p,p-DDD, p,p-DDT, dieldrin, lindane, endrin, α-endosulfan were found in these samples. These results show a rather homogeneous deposition and provision of sediments in estuaries from this zone. Both p,p-DDE and dieldrin are found with higher concentrations in the

TABLE 4. RESIDUES OF ORGANOCHLORINE PESTICIDES IN STRATIFIED SEDIMENT SAMPLES TAKEN IN 1996

Section of sediment core (cm)	Organochlorine pesticides detected (µg. kg $^{-1}$).						
	Lindane	A-Endosulphane.	Endrin	Dieldrin	pp'-DDT	pp'-DDE	pp'-DDD
0-5	6.21	ND	1.04	4.92	5.48	64.69	6.91
5-10	5.85	0.66	ND	2.18	2.84	49.28	4.89
10-15	3.98	0.59	0.49	8.91	2.18	44.57	3.48
15-20	4.27	ND	0.74	19.14	1.71	44.55	2.79
20-26	5.57	0.29	0.89	22.36	2.65	82.24	5.55
26-32	0.83	0.77	ND	1.46	2.58	47.59	7.63

ND Not detected

layer from 20 to 26 cm. Above this level pesticide concentrations are homogenous probably due to the continuous deposition of the sediments. Geographical distribution of the pesticide contaminated sediment is shown in Fig 2.

Shin et al. [4] investigated the adsorption of DDT by soils of different types and by isolated soil fractions. A sandy loam, a clay soil and a high organic muck . Adsorption was least in the sandy loam and greatest in the muck (distribution coefficients [kd] were in the ratio 1:10:80 for sandy loam, clay soil and organic muck respectively).

3.2. Pesticide residues in biological tissues

The highest concentrations of p,p-DDE (118.64 $\mu g.kg^{-1}$) and α-endosulfan (4.13 $\mu g.kg^{-1}$) were found in tissues of lisa fish (*Rajidae spp)* from Monte Redondo. Also, high concentrations of p,p-DDE (77.62 $\mu g.kg^{-1}$) and p,p-DDD (3.63 $\mu g.kg^{-1}$) were found in pargo fish (*Sparidae spp)* from the same site. These results show that Atoya River and its tributaries have contaminated the Naranjo estuary and aquatic life in it. the data also suggest a direct relationship between the pesticide contamination in the aquatic life and the sediment at this site

Analysis of clams (*Anadara spp)* taken from Realejo showed residues of pp-DDE (44.25 $\mu g.kg^{-1}$, α-BHC (8.86 $\mu g.kg^{-1}$) and p,p-DDD (7.29 $\mu g.kg^{-}$). These residues may be a result of the feeding

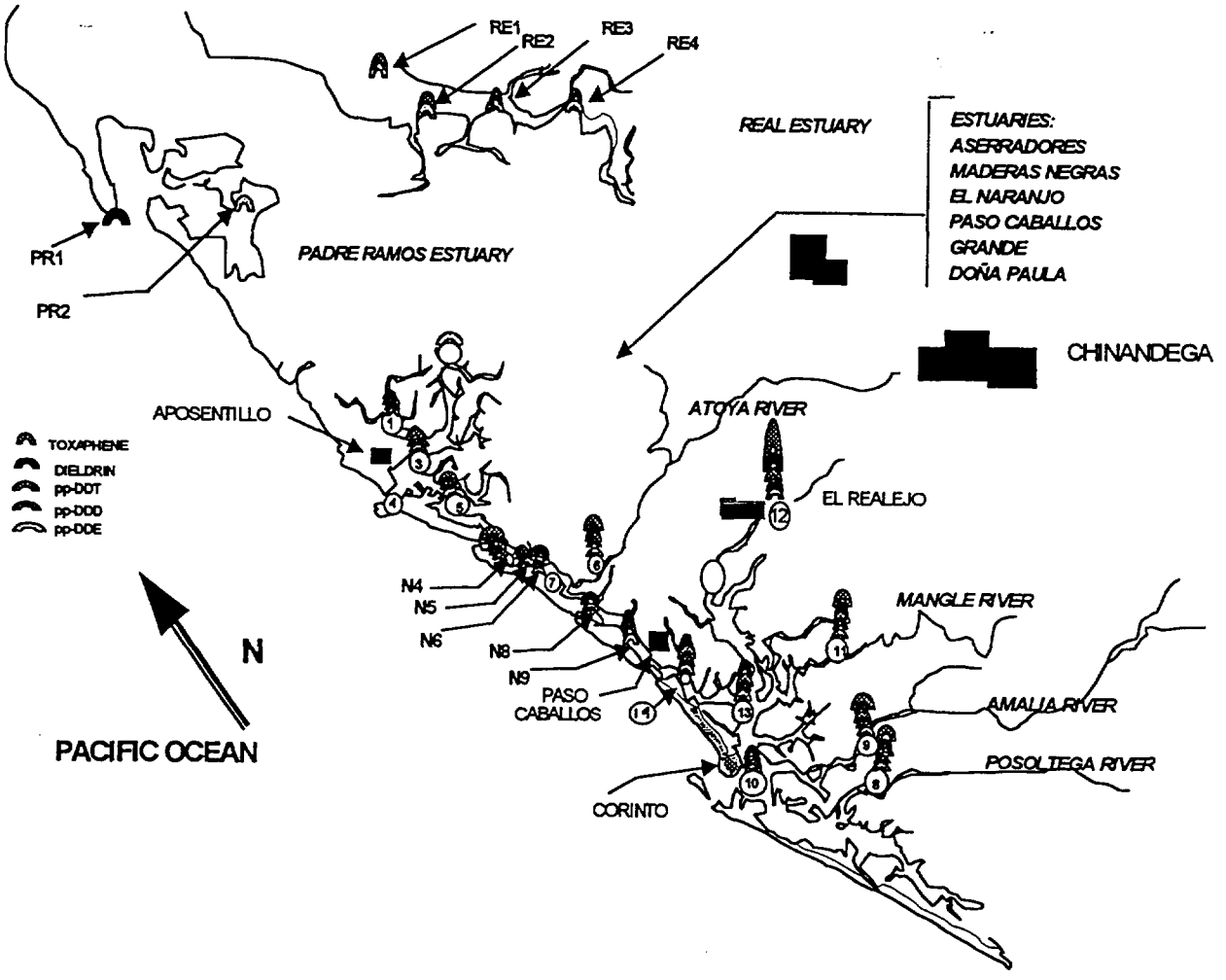

Fig. 2. Map showing distribution of organochlorine pesticides in surface sediment

behaviour of these organisms because they obtain their food through filtration, hence they are good indicators of contamination. Residues of p,p-DDE (38.78 $\mu g.kg^{-1}$), p,p-DDD (6.58 $\mu g.kg^{-1}$) and low levels of aldrin and heptachlor epoxide were also found in clams in La Lapa estuary.
The physical-chemical properties of DDT and its metabolites enable these compounds to be taken up readily by organisms. The rates of acumulation varies with the species, the duration and concentration of exposure, and with environmental conditions [2]. Different organisms metabolize DDT via different metabolic pathways. It may result in the formation of DDE or TDE. DDE is the more persistent metabolite, although not all organisms produce DDE from DDT. The alternative metabolism via TDE leads to more rapid elimination. Much of the retained DDT and its metabolites are known to store in lipid-rich tissues.

Other pesticides such as p,p-DDD, aldrin, α-endosulfan, heptachlor and α-BHC were also found in these tissues. The sampling site El Realejo shows the highest incidence of pesticides which correlate well with the sediment results. Organisms can acumulate these chemicals from the surrounding medium and from food. In aquatic organisms, uptake from the water is generally more important, whereas, in terrestrial fauna, food provides the major source. In general, organisms at higher trophic levels tend to contain more DDT-type of compounds than those at lower trophic levels.

4. CONCLUSIONS

The levels of contamination by organochorine pesticides found in different matrices in the second and third sampling journey show the advanced damage of a big area of the coastal lagoons in the western region of Nicaragua. This demonstrates an extensive use of these agrochemicals in past decades, which arrive with the runoff of cultivated soils to these coastal lagoons. On the other hand, residues of these agrochemicals have also been transported to these coastal lagoons through the most important rivers of the region, since, these rivers go through vast cultivated areas affected by erosion and human settlement. This contributes to the modification of the natural equilibrium of these aquatic ecosystems. The use of persistent organochlorine pesticides in cotton and sugar cane cultivation in the past has resulted in the contamination of aquatic life and sediment in the rivers and estuaries monitored. It can be concluded that the most contaminated sites in this area were Atoya River (site 6) and Posoltega River (site 8). The Atoya River is highly contaminated because it flows through the whole Chinandega Department, carrying along all kind of contaminants and especially residues of pesticides that were used in cotton cultivation. The confluence of Atoya River with Sasama, Acome and El Chiquito River; is another factor that has contributed to its contamination. Posoltega River has a large area of to runoff zones where the most important agricultural activity has been the cotton cultivation. It can be concluded from this study that all matrices of the coastal lagoon ecosystem are contaminated with the organochlorine pesticides resulting in an increase in damage to the coastal lagoon systems in the northwest region of Nicaragua.

REFERENCES

[1] VILLENEUVE, J.P., Personnel communication (Training Course on the Measurements of Organochlorine and Petroleum Hydrocarbons in Environmental Samples. IAEA-MEL/MESL (1995).

[2] WORLD HEALTH ORGANIZATION, DDT and its Derivatives - Environmental Aspects, (1989).
[3] ALBONE, E.S., G. ELINGTON, N.C. EVANS, J.M. HUNTER, M.M. REHEAD. Fate of DDT in severn estuary sediments. Environ. Sci. Technol., (1972):914-919.
[4] SHIN, Y.O., J. J. CHODAN, A.R. WOLCOTT, Adsorption of DDT by soils, soils fractions and biological materials. J. Agric. food Chem., (1970):1129-1133.