

## Final Report

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**Title: Well and Interstitial Water Crop Protection Chemicals in the Salinas Fan Delta Aquifer**

**Investigators:** José A. Dumas-Rodríguez and Rafael Montalvo-Zapata, Crop Protection Department, Agricultural Sciences College, University of Puerto Rico, Mayagüez Campus.

**Focus Categories:** TS, WQL, WL

**Congressional District:** (N/A)

### **Statements of the critical water problems:**

Jobos Bay is located between the Salinas and Guayama municipalities on the south coast of Puerto Rico and comprises more than 2,800 acres, including a forest and a mangrove. The Jobos Estuaries Ecosystem has been severely stressed since the late 80s by land and water channel alterations which have changed the water flow patterns of the zone. The presence and movement of toxic organic compounds in the JBNERR soils and groundwater need to be studied to assess their impact over flora, fish and wildlife. This project examined the groundwater water quality, toxic substances and non-point contamination in the JBNERR.

Non-managed application of organic compounds such as pesticides may reach non target sites and result in leaving residues in sites where they may reach surface and ground water resources. This study was the first intensive research related to organic pollution in the Jobos mangrove zone that provided a more comprehensive view of the zone water quality.

### **Statements of the results or benefits:**

The benefits of this study were that it allowed to obtain new scientific information related to pesticide and other toxic organic and inorganic residues in groundwater from JBNERR, Las Mareas and Aguirre Forest. Urban, industrial and agricultural developments are expected to increase in this zone. Therefore, these results must help

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an environmental sound development of the region. The project will also provide risk/benefit data for decisions concerning chemical usage. In addition, findings of this study were submitted to a referred journal and technical presentations to stakeholders such as the Land Authority of the Department of Agriculture and Natural Resources and Environmental Department representatives were done. This work was also presented in symposiums, and in national and international meetings such as SOPCA, AIDIS and CFCS.

## Methodology:

### Sample collection, preservation and handling

Pollutant analyses were conducted at the Agricultural Experiment Station Pesticide Laboratory. Replicated water samples were collected from fifteen wells from agricultural growing areas of the Jobos basin zone, and from twenty-five piezometers on the Jobos Reserve (Table 1 and 2).

Table 1. Wells Identification and Sector Location and Geographic Position

Well No	Well id	Sector	North			West		
			17°	58'		66°	13'	524"
W1	Aguirre 2	Aguirre	17°	58'	049"	66°	13'	524"
W2	Aguirre 3	Aguirre	17°	57'	901"	66°	15'	121"
W3	Esperanza	Esperanza	17°	57'	632"	66°	15'	271"
W4	Salich	Salich	17°	57'	638"	66°	16'	115"
W5	Vasquez	Las Mareas	ND					
W6	Soler1	Fortuna	17°	58'	127"	66°	15'	150"
W7	Jaguas 1	Jaguas	17°	58'	696"	66°	15'	690"
W8	Jaguas 2	Jaguas	17°	58'	737"	66°	15'	872"
W9	Vega	Fortuna	17°	58'	264"	66°	15'	437"
W10	Gonzalez	Fortuna	17°	59'	363"	66°	16'	275"
W11	Gonzalez Grua	Fortuna	17°	58'	801"	66°	15'	262"
W12	Gonzalez Antena	Fortuna	17°	58'	683"	66°	14'	961"
W13	Lanausse 1	Aguirre	17°	58'	747"	66°	14'	752"
W14	Lanausse 2	Aguirre	17°	59'	160"	66°	14'	757"
W15	Gonzalez Antena 2	Fortuna	17°	58'	801"	66°	15'	262"

ND-No determined

Piezometers were placed at the north, west and east zones of Jobos Basin, parallel to the abandoned stream channel and in the Esmeralda fault, north of the bedrock hill at the Aguirre sugar mill. The selected sampling wells and piezometers



were sited by GPS. Water samples were taken monthly for one year. Triplicate samples were collected in one-liter dark-brown glass bottles with Teflon lined caps (pre-washed

Table 2. Piezometer Identification, Sector Location and Geographic Position

<b>Piezometer id</b>	<b>Sector</b>	<b>Location</b>	<b>North</b>		<b>West</b>		
P1S1	S1	Aguirre Forest	17° 57'	442"	66°	13'	141"
P2S1	S1	Aguirre Forest	17° 57'	432"	66°	13'	151"
P3S1	S1	Aguirre Forest	17° 57'	421"	66°	13'	149"
P4S1	S1	Aguirre Forest	17° 57'	478"	66°	13'	159"
P5S1	S1	Aguirre South	17° 57'	490"	66°	13'	183"
P6S1	S1	Aguirre South	17° 57'	515"	66°	13'	198"
P7S1	S1	Aguirre South	17° 57'	519"	66°	13'	216"
P1S2	S2	Aguirre South	17° 57'	110"	66°	14'	853"
P2S2	S2	Aguirre South	17° 57'	0"	66°	14'	841"
P3S2	S2	Aguirre South	17° 57'	19"	66°	14'	870"
P4S2	S2	Aguirre South	17° 57'	001"	66°	14'	865"
P5S2	S2	Aguirre South	17° 56'	984"	66°	14'	846"
P1S3	S3	Las Mareas	17° 57'	64"	66°	15'	710"
P2S3	S3	Las Mareas	17° 57'	29"	66°	15'	672"
P3S3	S3	Las Mareas	17° 57'	15"	66°	15'	673"
P4S3	S3	Las Mareas	17° 57'	068"	66°	15'	735"
P5S3	S3	Las Mareas	17° 57'	001"	66°	15'	665"
P1S4	S4	Aguirre	17° 57'	207"	66°	14'	846"
P2S4	S4	Aguirre	17° 57'	215"	66°	14'	847"
P3S4	S4	Aguirre	17° 57'	221"	66°	14'	846"
P4S4	S4	Aguirre	17° 57'	188"	66°	14'	851"
P5S4	S4	Aguirre	17° 57'	173"	66°	14'	854"
P6S4	S4	Aguirre	17° 57'	164"	66°	14'	846"
P7S4	S4	Aguirre	17° 57'	181"	66°	14'	839"
P8S4	S4	Aguirre	17° 57'	186"	66°	14'	853"

with detergent and hot tap water, rinsed with distilled and de-ionized water, and dried in an oven at 400° C for 1 h). All water samples were placed in an ice chest at around 4° C and transferred to the Central Analytical and Pesticide Laboratories at Rio Piedras on the same collecting day. Sodium thiosulphate and copper metal (80 mg/L) were added as needed to remove residual chlorine and sulfur, respectively. The samples were stored at 4° C in a refrigerator from the time of collection until extraction, which was done the next day after collection. All water samples were filtered through a Whatman GB/F filter, followed by a Nylon membrane filter before chemical analysis.

### **Ammonium, nitrate, nitrite, pH, conductivity and phosphate determinations**

These chemical analyses were conducted at the Central Analytical Laboratory in Rio Piedras. Ammonium, nitrate and nitrite were analyzed by using the EPA method 353.2. Phosphate was analyzed by the EPA method 365.1. The water samples were preserved at 4° C with diluted sulfuric acid to pH <2 until the analysis.

### **Dissolved trace metal analysis**

Standard AOAC method 974.27 was used for analysis of Zn, Fe, Pb and Cu by Atomic Absorption spectrophotometry (AA).

### **Soil microbial biomass C and N**

Soil core samples were collected from the selected sampling sites for interstitial water monitoring (S1, S2, S3 and S4). The selected areas were in the north, west and east of Jobos basin zones; near the Rio Nigua, parallel to the abandoned stream channel, and in the Esmeralda fault, north of the bedrock hill at Aguirre Sugar Mill. Soil samples were placed in plastic bags, transferred to Rio Piedras, and then dried at 40° C. A 100 g sub-sample of soil were re-wetted to 15% moisture to stimulate microbial activity, and then incubated at 25° C for 5 days. Soil microbial biomass C was determined by fumigation incubation by exposing 40 -g soil samples rewetted and incubated for 5 d to alcohol free CHCl<sub>3</sub> vapor for 24 h. The vapors were evacuated and removed. The soil samples were incubated in a 1-L gas-tight glass container for 10 days at 25° C. The evolved carbon dioxide was trapped in 1N KOH and determined by titration with 1N HCL. The quantity of CO<sub>2</sub>-C was divided by an efficiency factor of 0.41 to calculate microbial biomass C (Anderson, 1982; Haney, 2000).

Soil microbial biomass N was determined by analyzing NH<sub>4</sub>-N concentration of fumigated samples following 10-d incubation period minus initial NH<sub>4</sub>-N prior fumigation, divided by an efficiency factor of 0.41. The NH<sub>4</sub>-N was extracted from 7 -g soil sample using 28 ml of 2M KCl. Samples were shaken for 30 min in a reciprocal shaker and filtered, and the extracts were analyzed for NH<sub>4</sub>-N by using an autoanalyzer.



### **Determination of clay and organic carbon content**

Clay, sand, silt, plus inorganic and organic carbon contents were determined by using standard methods reported elsewhere (Blake, 1965). Sampling plots were from all areas which the soil samples for microbial analyses were collected.

### **Adsorption-desorption studies**

Adsorptions were expressed as k-Freundlich values. A stock solution of 40 ppm in distilled and de-ionized water was prepared for ametryne by using Mangle Muerto and Sorgo soil collected in the selected plot area mentioned. Concentrations of 0.5, 1, 5, 10, 20, 40 ppm were prepared by dilution with 0.01N CaCl<sub>2</sub> solution using distilled and de-ionized water. Batch equilibrium sorption and desorption isotherms were obtained for ametryne in both soils (Liu, 1997). The laboratory tests were conducted by treating 1 g of air dried soil with 10 ml of the selected compound solution in a sealed test tube. The suspensions were protected from light with aluminum paper, kept at 22° C, and placed in a shaker for 24 h. Then, they were centrifuged for 10 min at 2500 rpm and a 5 -ml aliquot of the clear supernatant solution was analyzed with a HPLC system coupled to a UV/vis detector. The adsorption curves for pesticides and k- values were determined by use Freundlich model.

### **Point of zero salt effect (pzse)**

Potentiometric titration method at three different ionic strengths was used for measuring pzse from soils collected in Mangle Muerto, Bosque Aguirre, Sorgo and Las Mareas study areas. The batch method outlined elsewhere was used to calculate pzse (Sparks, 1982).

### **Statistical analyses**

One-way analysis of variances (ANOVA) was carried out using XLSTAT 7.5 data analysis computer software to compare the concentrations of metals, nutrients and conductivity at different interstitial water sampling sites in JBNERR and Aguirre forest.

The Tukey test was used to determine differences among sampling sites in metal, nutrient concentrations and conductivities.

### **Principal Findings and Significance:**

Intensive human activities in the municipalities of Salinas-Guayama are very close to JBNERR, an important threatened natural reserve from Salinas. Agriculture, dumping, Junker businesses and excessive ground water demands are some of the problems that are threatening groundwater quality in Salinas. Groundwater is the main source of freshwater for JBNERR and Aguirre Forest. Four monitoring zones were selected for determining groundwater quality between JBNERR and Aguirre Forest. Monitoring zones named S2, S3 and S4 were in JBNERR and S1 was in Aguirre Forest. The central and west zones (S2, S3 and S4) were located close to intensively cultivated fields with banana, plantain, papaya, sorghum, sunflower, soybean and other agricultural commodities upstream and S1 was close to the old Aguirre Sugar Mill and urban developments. The south-central zone (S2) was mangrove dieback area, and the southern area was a salt flat zone (S3) (Figure 1). The northern-central zone (S4) was intensely growing sorghum field.

During the April 2002 to February 2003 period, water samples were collected to determine pH, conductivity, NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>, TOC, TC, IC, Zn, Fe, Pb, Cu, toxic organic compounds and pesticides. The water samples showed a high content of organic compounds, and many of them were long chain hydrocarbons and alcohols as identified by GC-MS.

Some groundwater samples from the central zone of JBNERR resulted in positive detection of the organochloride insecticides lindane ( $\gamma$  BHC) and pentachlorophenol (PCP). The insecticides and wood preservative, respectively, were extensively used in the sugarcane plantations and wood treatment about 40 years ago. Herbicides such as atrazine, ametryne and monuron, the fungicide o-phenylphenol and the plant regulator diphenylamine (Coraza) were detected in the interstitial water (table 3). Atrazine was found in piezometers from S4 monitoring zone at levels of 0.5ug/L. This was because S4 piezometers were near to an abandoned sorghum growing area.





**EXPLANATION**

- S1, S2, S3, and S4 -Monitoring zones where piezometers were sunk

Figure 1. Jobos Bay interstitial water-collection sites in the study area in Salinas Puerto Rico

Other pesticides traces could not be quantified. Pesticide traces were found in groundwater from piezometers in JBNERR but not in piezometers from Aguirre Forest. Table 3 shows other harmful compounds such as N-methylformamide, 1,2-benzene dicarboxylic acid, diethyl ester, and benzene alcohol also found in groundwater. All monitoring zones had few mangroves growing or had mangrove dieback problems, except Aguirre Forest (S1).

Table 3. Summary of results of wells and piezometers sampled for recognized and suspected human hazard contaminants

Chemical	CASRN	use or type	frequency (%)	
			well <sup>a</sup>	Piezometer <sup>b</sup>
1_Tetradecanol (ALFOL 14)	112_72_1	hair tonics	16	9
Acetophenone	98-86-2	fragrance	1	19
(Capric acid) Decanoic acid	334_48_5	pesticide	3	3
(Coraza, Shield) Benzeneamine, N-phenyl	122-39-4	pesticide	3	8
Caffeine	58-08-2	stimulant	0	11

Chemical	CASRN	use or type	frequency (%)	
			well <sup>a</sup>	Piezometer <sup>b</sup>
(Muscalure) 9-tricosene, (Z)-	27519-02-4	pesticide	1	1
methanone, diphenyl	119-61-9	comestic	3	0
camphor	76-22-2	analgesic	1	0
(E)-tricos-9-ene	35857-62-6	pesticide	0	1
phenanthrene	85-01-8	PAH	0	1
Phosphoric acid, tributyl ester	126-73-8	herbicide	1	6
1,2-benzenedicarboxylic acid, butyl phenol	85-68-7	plasticizer	5	7
1,2-Benzenedicarboxylic acid, diethyl ester	84_66_2	plasticizer	2	1
Bisphenol A	80-05-7	plastic and printing	0	5
Nonylphenol	25154-52-3	detergent	6	8
phenol,2-(1,1-dimethylethyl)-4methyl)	2409-55-4	---	1	0
Phenol,4-chloro-3-methyl	59-50-7	pesticide	0	1
Di(2-ethylhexyl)adipate	103-23-1	plasticizer	0	1
( P-Cresol) Phenol,4-methyl	106-44-5	Paint	1	0
(-lindane) D-BHC	319-84-6	pesticide	0	2
Ametryne	834-12-8	herbicide	0	1
Benzaldehyde, 4-hydroxy-3-methoxy	121-33-5	---	1	1
1,2-Benzenediol, 4-(1,1-dimethylethyl)	98-29-3	printing	1	4
1,3-Isobenzofurandione	85-44-9	rubber and paint	0	1
O-Phenylphenol	90-43-7	Bactericides	0	2
Benzophenone	119-61-9	hair product, ink	0	1
Anthraquinone	84-65-1	---	0	1
Monuron	150-68-5	herbicide	0	1
Methanone (2-hydroxy-4-ethoxyphenyl)phenone	131-57-7	paint and plastic	0	1
Benzeneamine, N- nitroso-N-phenyl	86-30-6	rubber	2	0
formamide	123-39-7	---	3	4
octyl phenol isomer	1806-26-4	---	2	2
Atrazine	1912-24-9	herbicide	1	2
Amphetamine	300-62-9	stimulant	0	2
PCP	87-86-5	pesticide	0	2

<sup>a</sup>well samples No. - 77

<sup>b</sup>piezometer samples No. - 172



Table 4 showed a summary of the annual average levels of heavy metals in groundwater from JBNERR and Aguirre Forest monitoring zones.

Table 4. Summary of average of the average values found for inorganic contaminants in interstitial water

Statistical	Pb (µg/ml)	NH <sub>4</sub> (µg/ml)	NO <sub>3</sub> (µg/ml)	Cu (µg/ml)	Zn (µg/ml)	Fe (µg/ml)	PO <sub>4</sub> (µg/ml)
Mean	0.78	1.43	0.72	0.15	0.07	0.58	3.85
std dev.	0.49	1.47	1.09	0.17	0.06	0.52	6.61
Maximum ave. value	1.69	4.95	3.75	0.58	0.20	1.74	20.00

We found nitrate levels between 0.11 and 5.00µg/mL in groundwater samples from S4 monitoring zone. The higher nitrate levels were from those piezometers closest to a sorghum growing area. Phosphorus levels in Aguirre Forest (S1) were between 0.5 and 30 µg/m, which is over the environmental background level of 0.03µg/ml. Lead, cooper and zinc were detected in some groundwater samples from JBNERR and Aguirre Forest. Lead levels were between 0.11 and 1.69, as compared to environmental background of 0.015µg/ml; copper levels were between 0.03 and 0.58µg/ml; and zinc levels were between 0.05 and 0.37 µg/ml.

Comparison of lead, zinc, iron and cooper showed some significant differences among the four samplng sites. We found that lead was significantly lower (α=0.05) for S4 than for the other sites; the zinc was significantly lower for S1 and S4 than for the other sites. Iron was significant lower for S4, followed by S1; the amount of copper was similar for sites S1 and S4 and similar for sites S1 and S3 at a level of significance of 0.05. This mosaic-like pattern is caused by the difference in lead, zinc, iron and cooper environmental behavior.

The S4 had a significant lower annual mean EC than the other sites (Table 5). This finding may account for the low mean dissolved trace metal found in the S4 site because of the low water soluble chlorine complex formation.

Table 5. pH and conductivity Annual Average in groundwater samples from JBNERR and Aguirre Forest<sup>1</sup>.

Site	pH	Conductivity ( $\mu\text{S cm}^{-1}$ )
S1	7.59 (0.29) <sup>a</sup>	120206 (62539) <sup>a</sup>
S2	7.55 (0.29) <sup>a</sup>	154686 (74769) <sup>b</sup>
S3	7.63 (0.24) <sup>a</sup>	126832 (94686) <sup>a,b</sup>
S4	8.25 (0.28) <sup>b</sup>	2471 (1369) <sup>c</sup>

<sup>1</sup>Standard deviations are shown in parentheses. The number of replications were between 28 and 45. Values with different letters within a column are significantly different at 0.05 (Tukey test).

The increased water concentration of lead in S1, S2 and S3 sites may be due to complexes formations with abundant dissolved humic matter in mangrove forest. Lead also had a high correlation coefficient with EC because salinity may increase complex formations of lead with organic matter and thus increased the lead desorption from sediment surfaces (Kennish, 1998; Bryan et al, 1992). Iron, zinc, and copper form chlorine-metal complexes; therefore an increase in EC may increases their water concentrations (Table 6).

Table 6. Simple correlation coefficients between the annual mean of heavy metal concentrations and the annual mean of electric conductivities for the four sampling sites in JBNERR and Aguirre forest.

Element	R <sup>2+</sup>
Pb	0.9773
Zn	0.9356
Fe	0.8295
Cu	0.7928

\*Significant at the 5% level.

The highest groundwater water pH was in the S4 monitoring area ranging between 8.0 and 8.4. The other monitoring zones had groundwater whose pH values ranging between 7.3 and 8.0. Strong differences in the amount of dissolved oxygen (DO) in the interstitial water were observed among the four selected monitoring zones.



No detectable DO levels were found in S1 monitoring zone (Aguirre Forest). Groundwater samples from S2 and S3 zones had levels between 23 and 66, and 10 and 39 mg/L, respectively. The higher DO levels were observed in groundwater samples from S4 monitoring zone, whose levels ranging between 70 and 82 mg/L. Low DO levels in the S1 monitoring zone was because S4 had a high amount of dissolved organic matter (a healthy mangrove forest) decreasing available DO in water. The highest groundwater conductivities were found in S2 monitoring zone (165 mS/cm). This area had an average conductivity value higher than S3, a salt flat area (124 mS/cm). Bosque Aguirre (S1) and Sorgo (S4) had average interstitial water conductivity of 94 and 2.7 mS/cm, respectively.

Regarding groundwater from irrigation wells, upstream JBNERR and Aguirre Forest, the major contaminant was nitrate. Nitrate concentration showed a high variability with time probably due rainfall, irrigation rate and frequency of fertilizer application. Phosphate was not detected in samples from irrigation wells, thus suggesting that its presence in piezometers from Aguirre Forest comes from non agricultural sources. Lead, cooper and zinc were not detected in the sampled wells. Atrazine, a s-triazine herbicide was detected (below 0.1 µg/L) in some monitoring wells, and well as traces of pesticides such as diphenyl amine (Coraza) and 4-chloro-3methyl phenol (4-chloro-m-cresol) were detected (Table 3).

Soil samples from JBNERR and Aguirre Forest were analyzed for nutrients and heavy metal content, and the point of zero salt effect (pzse) (Table 7 and 8). Higher lead concentration was found in those soil samples from S3 (Las Mareas). This is a potential threat to human health because Las Mareas community is very close to S3 and must be carefully monitored. A very low organic matter content was found in S2 (Mangle Muerto -mangrove dieback area) compared to that of S1 (Aguirre Forest). This findings and the high pH compared to S1 is indirect data which suggest that a shifting of microbial fauna and flora may occur in the S2 area.

Laboratory tests were done to measure C and N microbial biomass in the four monitoring zones. Aguirre Forest, an area not affected by mangrove dieback, had higher C microbial biomass than the other sampling areas in Jobos Bay. This finding is in accord with healthy mangrove growing. However, N soil microbial biomass was lower

Table 7. Nutrient and Heavy Metal Content in Soils from the Four Monitoring Zones.

Sampling Place <sup>1/</sup>	P (ug kg <sup>-1</sup> )	Ca (%) <sup>2/</sup>	K (%) <sup>2/</sup>	Mg (ug/g) <sup>2/</sup>	Pb (ug/g) <sup>3/</sup>	Cd (ug/g) <sup>3/</sup>	Cu (ug/g) <sup>2/</sup>	NH <sub>4</sub> (ug/g) <sup>4/</sup>	NO <sub>3</sub> (ug/g) <sup>4/</sup>
S1	139 (±77)	0.63 (±0.11)	0.21 (±0.06)	0.57 (±0.20)	1.5	nd	0.61	14 (±4)	Nd
S2	42 (±14)	0.53 (±0.05)	0.20 (±0.02)	0.53 (±0.07)	nd	nd	—	20 (±4)	Nd
S3	44 (±16)	0.50 (±0.11)	0.13 (±0.03)	0.27 (±0.08)	160	nd	0.12	17 (±7)	12 (±17)
S4	24 (±4)	0.62 (±0.03)	0.04 (±0.01)	0.14 (±0.03)	0.87	nd	0.17	20 (±9)	12 (±6)

1/Samples collected from at least three points in the four monitoring zones in JBNERR and Aguirre Forest. Each area was replicated six time; 2/exchangeable cations (NH<sub>4</sub>OAc pH 7); 3/total; 4/exchangeable KCl 2N.

Table 8. Particle size analyses of soils from the Four Monitoring Zones.

Sampling Place <sup>1/</sup>	pH	M.O. (%)	N (%) <sup>2/</sup>	Cu (ug/g) <sup>2/</sup>	Zn (ug/g) <sup>2/</sup>	Fe (%) <sup>2/</sup>	Silt (%)	Lime (%)	Clay (%)
S1	7.7 (±0.3)	10.7 (±4.0)	0.25 (±0.11)	70 (±2)	102 (±51)	1.8	30 (±19)	57 (±13)	13 (±6)
S2	8.0(±0.2)	14.0(±8.50)	0.31 (±0.11)	44(±4)	53 (±9)	0.8	22 (±9)	58 (±7)	20 (±6)
S3	8.3 (±0.1)	2.3 (±1.3)	0.13 (±0.07)	73 (±8)	121 (±38)	0.1	24 (±14)	63 (±24)	13 (±10)
S4	8.4 (±0.5)	3.3 (±0.6)	0.18 (±0.03)	76(±3)	88 (±2)	1.6	36 (±8)	23 (±11)	41 (±8)

1/samples collected from at least three areas for each sampling place. Each area was replicated six time; 2/total

in Aguirre Forest than in the S2 area, a mangrove death zone. This finding suggests a potential ecosystem health threat (Table 9). A second confirmation trial showed higher levels of C microbial biomass, and had an N microbial biomass profile different from the first trial. The first trial had C microbial biomass between 120 and 190 cg kg<sup>-1</sup>. The N microbial biomass for the first trial was between non detectable and 25 mg kg<sup>-1</sup>. The second trial had C and N microbial biomass between 330 and 370 cg Kg<sup>-1</sup> and between 5 and 24 mg kg<sup>-1</sup>, respectively. Spatial variability and changes in the environmental conditions probably were responsible for differences between the first and second sampling (Table 9). The low range of N microbial biomass, especially in the S2 and S3 zones, is not typical of a healthy soil system and requires a more extensive study.



Table 9. Microbial biomass-C and N in the four selected sampling sites

Place	Second samples set	
	Average (cgCO <sub>2</sub> /Kg)	Average (mgNH <sub>4</sub> /kg)
S1	349 (±8)	14 (±13)
S2	370 (±40)	5 (±5)
S3	360 (±32)	8 (±4)
S4	330 (±13)	24 (±21)

values in parenthesis is 1s

The point of zero salt effect (pzse) was determined from soil samples taken in the four monitoring zones (S1, S2 S3 and S4). The potentiometric titration method was used for pzse study. Sodium chloride as indifferent salt was used to bring all samples to an equal state of saturation in order to compare soils. The point of zero salt effect was determined from the crossover point of net electric charge vs. pH curves for the soil studies at three ionic strengths (Fig. 2). To calculate net electric charge the equation 1 was used:

$$\Delta H - \Delta OH = [10^{-pH_B} - 10^{-pH_s}] - [10^{-(14-pH_B)} - 10^{-(14-pH_s)}] \times 100 / (W \times \gamma) \quad \text{equation 1}$$

where

$\Delta H - \Delta OH$  = proton surface charge density

pH<sub>B</sub> = pH of the blank solution

pH<sub>s</sub> = pH of the solution equilibrated with the sample

$\gamma$  = single ion activity coefficient calculated with the Davies equation

W = soil sample weight (g)

The pzse for Bosque Aguirre (8.0), Mangle Muerto (8.1), Las Mareas and Sorgo were 8.0, 8.1, 8.3 and 7.0, respectively. Bosque Aguirre had the lowest proton surface charge density changes with pH and Mangle Muerto the highest one. This is an important factor to figure out potential environmental effects of ionizable organic compounds, such as ametryne, an s-triazine basic herbicide frequently used in the bording areas of JBNERR and Las Mareas for crop protection. In addition these findings also pinpoint a better buffering capacity for Aguirre soils toward net charge changes with pH compared to the other soils.

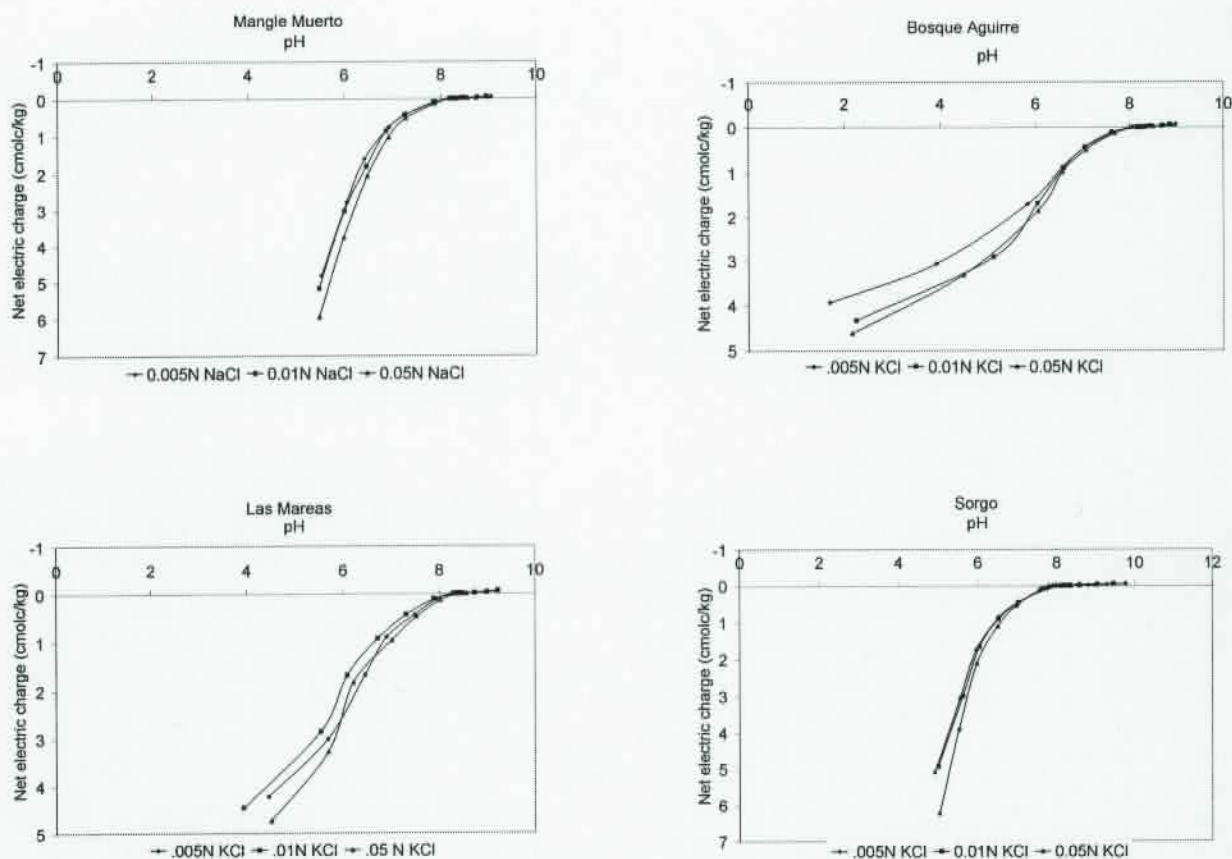


Figure 2. The pzse Bosque Aguirre, Sorgo, Mangle Muerto and Las Mareas soils as determined by potentiometric titration.

Ametryne was chosen as a model molecule to study the sorption of ionizable organic compounds soils from JBNERR and Aguirre Forest (Mangle Muerto, Sorgo, Las Mareas and Aguirre Forest soils). Figure 3 shown soil sorption curves of ametryne in above mentioned soils.

The  $K_d$  value is an important parameter governing mobility of the compound in the soil, where as  $K_d$  value increase the compound mobility decrease. The simple Freundlich equation 3 fitted the empirical data obtained (Fig.3).

The Freundlich isotherm equation is

$$\log C_s = \log K_d + 1/n \log C_e \quad \text{equation 2}$$



All isotherms had a c-type behavior which is in accord with a  $1/n$  value of 1 where the Freundlich expression becomes simply a distribution coefficient given by

$$C_s = K_d C_e$$

equation 3

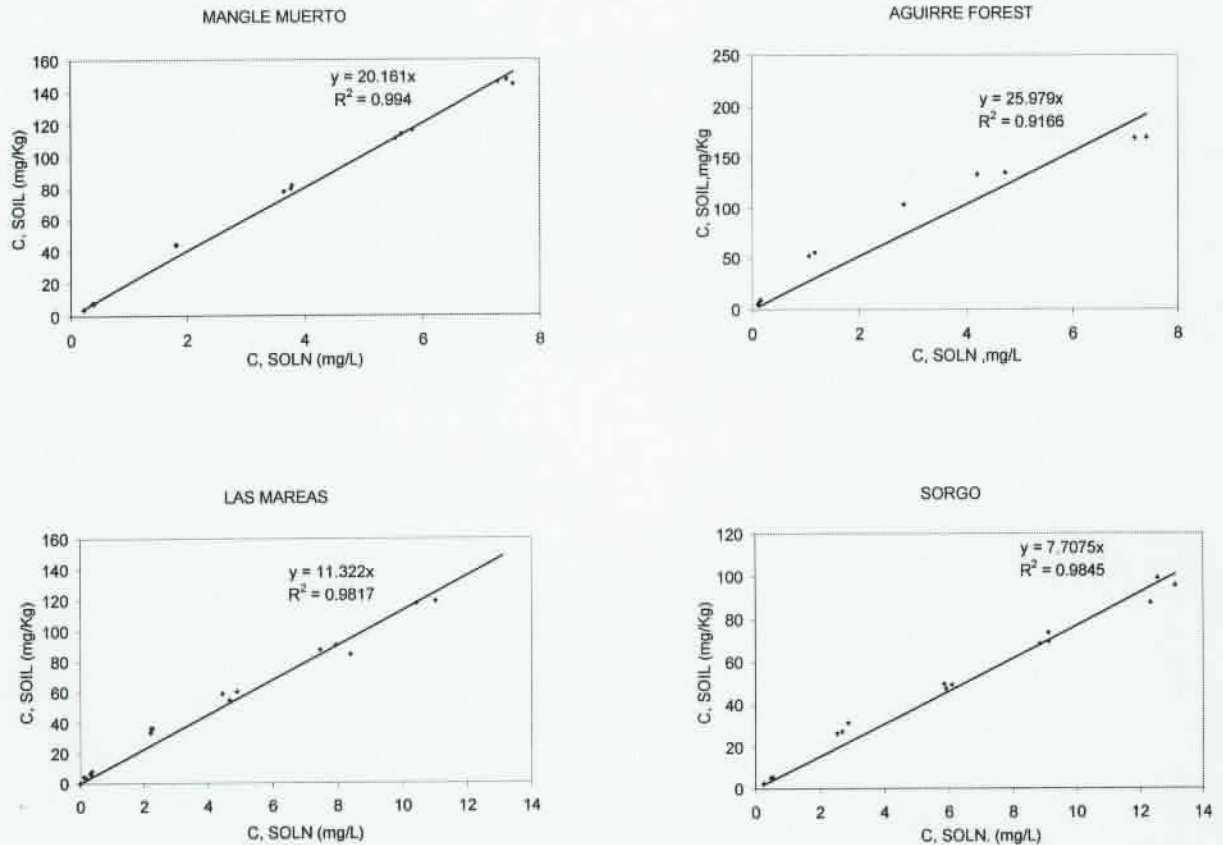


Figure 3. Freundlich adsorption isotherms for ametryne in Mangle Muerto, Aguirre Forest, Las Mareas and Sorgo Soils

The higher  $K_d$  value was obtained for Aguirre Forest Soil (26.0) and the lower was for Sorgo soil (7.7), all of which suggests a higher capacity of Aguirre Forest soil to adsorb and remove this compound from water. This finding is in accord with the proton adsorption graph mentioned above (Fig. 2) and showed the remarkable capacity of estuaries soil to retain toxic ionizable compounds. The adsorption-desorption behavior of organic compounds must be studied because it will determine environmental impact

of these compounds. Figure 4 shown desorption curves of ametryne for the four soils above mentioned.

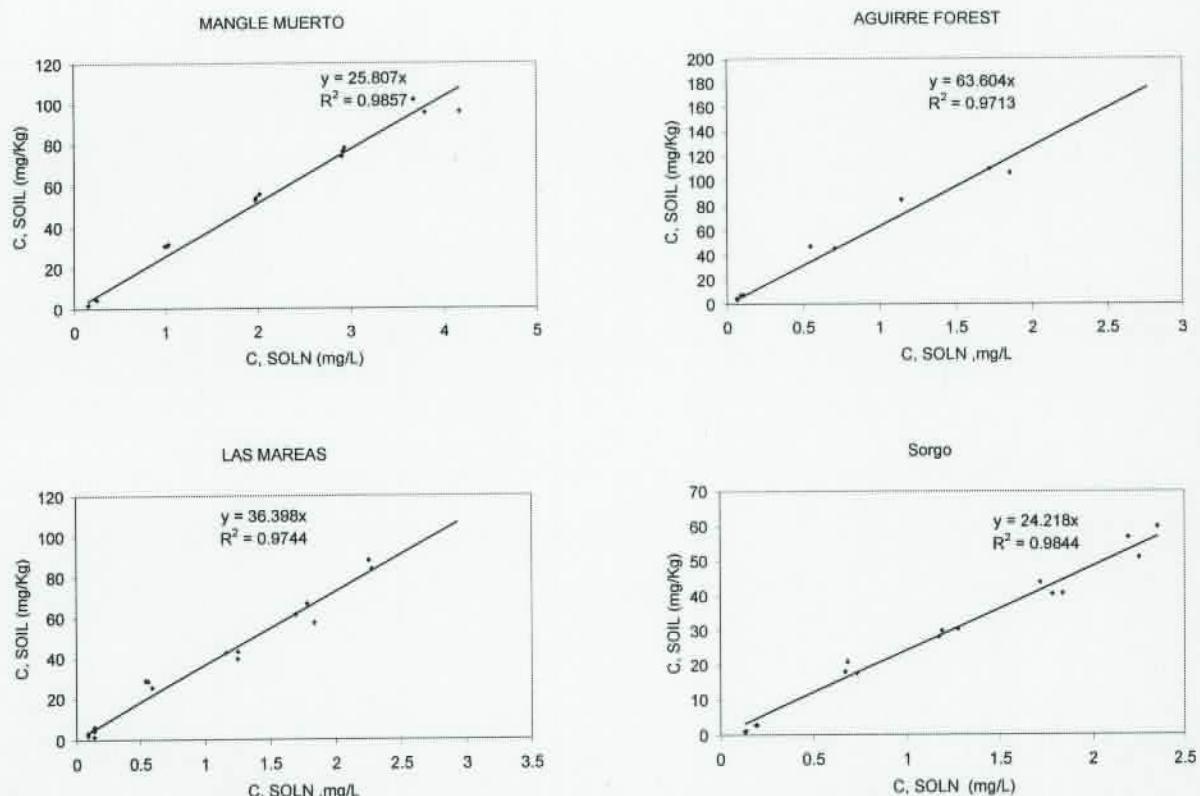


Figure 4. Freundlich desorption isotherm for ametryne in Mangle Muerto and Sorgo Soils (48 h).

We found a linear behavior that fitted well a Freundlich desorption model for all studied soils (Fig. 4). This behavior followed the simplified mathematical Freundlich desorption equation 4.

$$C_s = K_{des} C_e \quad \text{equation 4}$$

Ametryne had a pretty high  $K_{des}$  value for Aguirre soil compared to the other (Figure 4). Therefore, ametryne sorption interactions seem to be higher in Aguirre Forest soil been mostly irreversible while for Mangle Muerto soil was reversible. In addition, all  $K_{des}$  values were pretty higher than  $K_d$ , except for Mangle Muerto soil. This finding pinpoint lower kinetic for desorption than sorption for ametryne for Aguirre Forest, Las Mareas and Sorgo soils (hysteresis), but not Mangle Muerto soil.



The high number of anthropogenic organic compounds and high levels of trace metals found in the JBNERR are due to local sources such as the Salinas Thermoelectric plant, Salinas Dumping place, junk yards, agriculture and other activities conducted in the nearby areas. Black mangrove diebacks in the JBNERR have impaired the ecological balance. These conditions have increased trace metal mobility and may have affected organic pollutant entrance and mobility.

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### **Related Presentations and publications:**

- Dumas, J.A., R. Montalvo, and O. Rosario. 2003. Ground water quality under pineapple growing fields in Manati Quadrangle of Puerto Rico, A tropical Karst Zone; Well and interstitial water crop chemicals study on the Salinas Fan. Oral presentation. Asociacion Interamericana de Ingenieria Sanitaria y del Ambiente (AIDIS). Tropimar Convention Center. April 4.
- Dumas, J.A., R.Montalvo, P. Casanova, E. Rivera, N. Corchado, and Z. Nieto. 2002. Well and interstitial water study in the Salinas Fan. *Memorias Reunion Cientifica Anual SOPCA*, p30 (abstract-poster)
- Dumas J.A., R. Montalvo. 2003. Well and Interstitial Water Crop Protection Chemicals In the Salina Fan Delta Aquifer. *Simposio de Investigacion y Restauracion Estuarina*. 2-3 octubre. Wyndhan El San Juan Hotel y Casino. Isla Verde.
- Dumas, J. Casanova, P. Montalvo, R. 2004. Sorption and desorption of Ametryne in soils of Jobos Bay National Research Reserve and Aguirre Forest. *Memorias Reunion Cientifica Anual SOPCA*, p17 (abstract).
- Dumas, J. Montalvo, R. and Casanova, P. 2005. Saline effect in agrochemicals and heavy metals environmental distribution in Jobos Bay National Research Reserve. In: *Proc., 41st Annual Meeting Caribbean. Food Crops Soc.* In press.

Dumas, J. Montalvo, R. and Casanova, P., Rivera, E. and Corchado, N. 2005.  
Behavior of Nutrients, Heavy Metals and Anthropogenic Organic Compounds in  
Jobos Bay National Estuary Research Reserve and Aguirre Forest. Submitted to  
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