

Soil and interstitial water quality in Jobos Bay^{1,2}

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ABSTRACT

The Jobos Bay National Estuary Research Reserve (JBNERR) in Salinas, Puerto Rico, has served as sink for many anthropogenic substances that may affect the quality of the soil and water and the integrity of the biota. Four transects were established in the southeastern part of JBNERR for interstitial water collection. In addition, soil samples were collected from transects I, II, and III, at sites that were affected by runoff from a road closer to the Salinas landfill. The concentration of lead (Pb) in interstitial water from the above mentioned transects ranged from 0.07 to 0.68 mg/L; chromium (Cr) concentration ranged from 0.03 to 0.24 mg/L; and manganese (Mn) concentration ranged from 0.35 to 15.25 mg/L. The total Pb in soil samples ranged from 59 to 758 mg/kg, in an uneven distribution along transect II. The low Pb concentrations in water in comparison to that in soil indicate the high capacity of the JBNERR soils to serve as sink for heavy metals. The linear correlation between Pb concentrations in the interstitial water and the electrical conductivity suggests that marine water increases Pb remobilization from soils. Also detected in interstitial water were anthropogenic organic compounds such as benzothiazole, 1-methyl-2-pyrrolidinone and tert-butyl phenol; however no residues of pesticides used from agricultural farms nearby were found. Results have shown that human activities have affected soil and water quality in the JBNERR.

Key words: soil and water quality, estuary, contamination, anthropogenic compounds

RESUMEN

Calidad de los suelos y del agua intersticial en la Bahía de Jobos en Puerto Rico

La Reserva Nacional de Investigación Estuarina de Bahía de Jobos (RNIEBJ) en Salinas, Puerto Rico, ha sido sumidero de muchas sustancias

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antropogénicas que pueden afectar la calidad del suelo y del agua y la integridad de la biota. Se establecieron cuatro transectos en la parte sureste de RNIEBJ para la recolección de agua intersticial. Además, se recolectaron muestras de suelos en los transectos I, II y III, en lugares afectados por la escorrentía de un camino cercano al vertedero de Salinas. La concentración de plomo (Pb) en el agua intersticial varió entre 0.07 y 0.68 mg/L; la concentración de cromo (Cr) osciló entre 0.03 y 0.24 mg/L; y la concentración de manganeso (Mn) varió entre 0.35 y 15.25 mg/L. El Pb total en muestras de suelo varió entre 59 y 758 mg/kg en una distribución desigual a lo largo del segundo transecto. Las concentraciones bajas de Pb en el agua intersticial en comparación con las del suelo indican la alta capacidad de retener metales pesados que tienen los suelos de RNIEBJ. La correlación lineal entre las concentraciones de Pb en el agua intersticial y la conductividad eléctrica sugiere que el agua marina incrementó la remoción de Pb de los sedimentos. Además, en el agua intersticial se detectaron compuestos orgánicos antropogénicos, tales como benzotiazol, 1-metil-2-pirrolidona y tert-butil fenol, pero no se detectaron residuos de los plaguicidas utilizados en las fincas agrícolas cercanas. Los resultados han mostrado que las actividades humanas han afectado tanto la calidad de los suelos como la calidad del agua en RNIEBJ.

Palabras clave: calidad de suelos y agua, estuario, compuestos antropogénicos

INTRODUCTION

Jobos Bay is located between Salinas and Guayama municipalities on the south coast of Puerto Rico and comprises more than 1,012 ha, including both the Aguirre Forest and Jobos Bay National Estuary Research Reserve (JBNERR). The JBNERR is the second largest mangrove forest in Puerto Rico; it is bordered by the Salinas Regional Waste Dump, a poultry processing plant on the east, agricultural and urban lands on north and west, the Salinas Thermoelectric Plant on the southeast, and the Caribbean Sea on the south (Figure 1).

The Salinas Fan Delta is the main source of fresh water in the JBNERR estuary (Gómez and Quiñones, 1990; Robles et al., 2003). This aquifer generally flows from north to south, and may transport soluble inorganic and organic contaminants to the coast. Two cones of depression caused by excessive groundwater withdrawals changed the flow in some areas in the middle 2000 (Rodríguez, 2006), affecting the hydrology of the aquifer. From 1986 to 2003, decline in the water table level of the aquifer promoted higher intrusion of marine water (Rodríguez, 2006). Groundwater pollution, marine water intrusion and dieback of the black mangrove in JBNERR are serious concerns to local and federal government agencies and to the Aguirre community in Puerto Rico (Rodríguez, 2006).

The Salinas Regional Waste Disposal Facility (SRWDF) is close to the JBNERR. The site where SRWDF is located has two types of soils

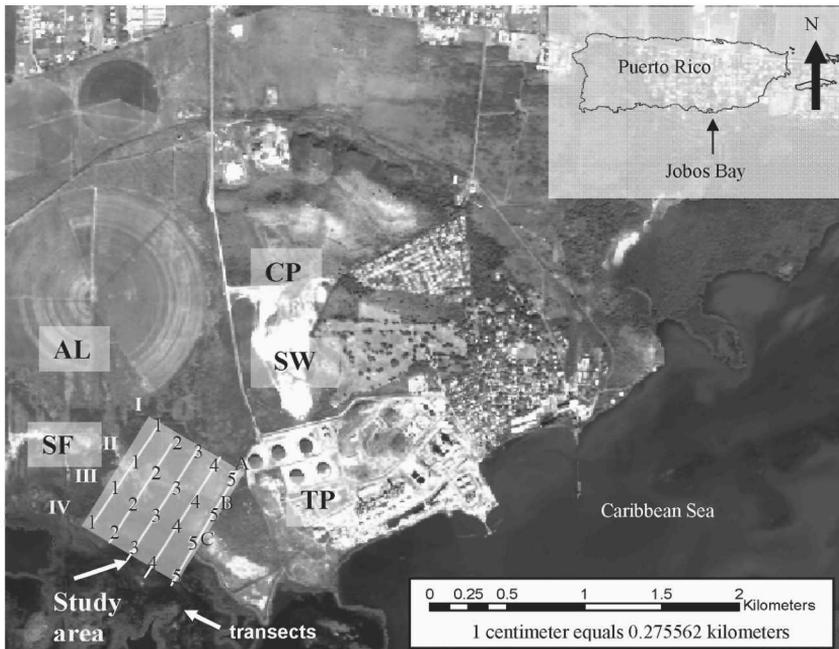


FIGURE 1. Aerial photo of Jobos Bay in Salinas, Puerto Rico, showing the study area and the groundwater sampling transects (--- I to IV). AL-agricultural lands; CP-chicken poultry; SW-Salinas Regional Waste Disposal; SF-abandoned sorghum farm; and TP-Thermoelectric Plant. The letters A, B and C in transects I, II and III indicate the sites for soil sampling in this study.

(Pozo Blanco and Jacana series) and rock land; thus layered/multiple hydraulic conductivities must be expected. The SRWDF may affect JBNERR and adjacent agricultural and community lands; therefore, it is necessary to assess the presence of toxic compounds. This solid waste landfill, as others, receives large quantities of heavy metals, which may affect adjacent resources in the long term (Aucott, 2008). The surface water flow pattern on the west side of SRWDF is toward the southwest; from the east side, towards the southeast. Therefore, these waters may reach several estuarine zones in Salinas. In case of heavy rainfall events, the runoff could reach JBNERR. The above scenario emphasizes the need for better knowledge for understanding water chemical quality in the JBNERR area. The main objective of this two-year study was to determine the groundwater quality and presence of agrochemicals, heavy metals and other toxic substances in JBNERR. The second objective was to study the effect of increased salinity in heavy metal release from JBNERR soils. This two-year study

was undertaken to determine the soil and groundwater quality in the eastern part of the JBNERR. Both field and laboratory research helped to provide a more comprehensive view of the effect of human activities on water quality in JBNERR.

MATERIALS AND METHODS

The JBNERR soils are alluvial deposits with some salt flats and marine water flooded areas. They consist of unconsolidated clay, silt and organic matter, and in the northern part of the Reserve they consist of unconsolidated sand, gravel and pebbles. Alkaline soil samples (pH 7.95 to 8.23) with high organic carbon content were obtained from the northeast part of the JBNERR. Three soil samples were taken at vertical spacing of 30 cm at sites A, B and C (Figure 1); these samples were placed in plastic bags and transported to the Pesticide Laboratory of the Agricultural Experiment Station in Río Piedras. Each sample was air-dried at room temperature, ground and passed through a 2 mm stainless steel sieve and analyzed for different physical and chemical characteristics. Soil organic matter was determined by the Walkley and Black method (Walkley and Black, 1934). Dry soil (10 g) was extracted with neutral 1M NH_4OAc at soil to solution ratio of 1:10 by shaking on a mechanical shaker for 30 min. The suspensions were filtered through Whatman 42 filter paper. The filtrates were analyzed for Na, K, Ca and Mg by atomic absorption (model SOLAAR 969; Thermo Jarrel Ash, Franklin, MA).⁵

Total extractable Pb was determined by microwave-assisted extraction (method 3052; USEPA, 1996). Soil (0.46 g) was extracted with 9 mL of concentrated HNO_3 in combination with 2 mL of HCl and 2 mL of HF. The suspensions were diluted to 50 mL, and then filtered through Whatman 42 filter paper. Acid soluble Pb was extracted with 0.1 N HCl at soil (10 g) to solution ratio of 1:10 by shaking on a mechanical shaker for 30 min. The suspensions were filtered through Whatman 42 filter paper. Both filtrates were analyzed for Pb by atomic absorption.

Water samples were collected between July 2004 and May 2005 from 20 piezometers (PVC pipes with 3-mm holes along 0.60 m long to allow water entrance) distributed along six transects (Figure 1). Piezometer depths ranged from 1.5 to 4.6 m in order to reach the water table of the aquifer. The piezometers were located by GPS (ScoutMaster™ GPS, Trimble Navigation). One-cm Teflon pipes along the length

⁵Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty or endorsement of equipment or materials by the Agricultural Experiment Station.

of the piezometer and a vacuum pump were used to collect water samples from piezometers. Water samples were collected, after purging the piezometer, in 1-L dark brown glass bottles with Teflon-lined caps (pre-washed with detergent and hot tap water, then rinsed with distilled and de-ionized water, and dried in an oven at 400° C for 1 h) and stored in a portable chest with blue ice to keep samples refrigerated until arrival at the Pesticide Laboratory. The samples were stored in a refrigerator at 4° C until the next day after collection, and then were filtered through a nylon membrane of 0.45 µm before chemical analysis.

The filtered samples were analyzed following the Standard AOAC method 974.27 (AOAC, 1990) for Pb, Cr, and Mn. Those samples with heavy metal concentrations higher than the National Recommended Water Quality Criteria (NRWQC) standard values (USEPA, 2002) were verified by the standard addition analysis method. For standard addition, samples were fortified at 0, 50, 100, 150, 200, and 400 µg/L with heavy metals above those using commercial atomic absorption standards (Fisher Co.). The concentration of the metal was calculated from the X-axis intercept from the plot of heavy metal added vs. response signal. Samples were analyzed by using an atomic absorption spectrophotometer. No significant differences were found between external standard and standard addition methods.

Standard EPA colorimetric methods 350.1 and 365.1 (Keith, 1996) were used for ammonia and o-phosphate analysis, respectively. The method for ammonium ion is based on the reaction of ammonium ions with salicylate and hypochlorite in the presence of sodium nitroprusside. The o-phosphate method is based on the formation of a blue molybdenum complex.

The effect of salinity on remobilization of Pb from JBNERR soil was studied by preparing artificial sea water from sea salt. The salinities levels ranged from 0 to 5, 10, 50 and 100‰. Major ion compositions of artificial seawater of 10‰ were 1676 mg/L of Na, 0.20 of Mg, 5.86 of Ca and 4.22 of K. Duplicate one-gram soil samples were left at room temperature in contact with 10 mL of the artificial seawater for seven days and then centrifuged at 10,000 rpm for 5 min. The supernatant was passed through a 0.45-µm nylon syringe filter and analyzed for Pb by using the AOAC method 974.27. Seawater did not present significant interferences with Pb measurements. Salinity observed in the salt flat area is usually 100‰, higher than 35.5‰ (Lugo et al., 2007), the average value observed in the top water in the Caribbean Sea (Hernández-Guerra and Joyce, 2000).

The effect of Pb sorption on the release of Ca from JBNERR soil was studied. Ten mL of Pb aqueous solutions [Pb(NO₃)₂] of concentrations ranging from 0 to 1, 2, 4 and 10 mg/L were added, each separately, to

1-g samples of JBNERR soil. The solutions were left to equilibrate for 1 h and then centrifuged at 10,000 rpm for 15 min. The supernatant was passed through a 0.45- μ m nylon syringe filter, and then measured for Ca content by atomic absorption.

Organic compounds were extracted by the SPE-disk method as outlined by Mersie et al. (2002). A 1-L water sample was passed through a pre conditioned Empore C18 disk and re-extracted in 5 mL of ethyl acetate. Analyses were performed by gas chromatography/mass spectrometry (Perkin Elmer GC/MS Autosystem-TurboMass) by using a 30 m \times 0.25 mm \times 0.10 μ m film thickness DB-5 capillary column with the following operating conditions: a temperature program of 3 min at 70° C; then increasing at 10° C/min to 250° C and holding for 3 min; 3 min solvent delay in MS and helium carrier gas at 1.0 mL/min flow rate. An injection of 1 μ L in an injection port set in splitless mode at 250° C was used. The mass spectrometer detector was set at total ion mode, range 50 to 450 amu. Compound identification was based on the retention times and molecular fragmentation spectra identification by using a Wiley mass spectra library.

RESULTS AND DISCUSSION

JBNERR sediments

Table 1 shows physicochemical properties of JBNERR soils from sites A, B and C (Figure 1). The significantly higher amounts of K and Na in site C are related to tidal flooding. Calcium was the major cation in soil samples because JBNERR is within the Salinas Fan Delta and alluvial deposits are rich in calcite (Robles et al., 2003).

Wetlands sediments are sink of heavy metals, from which Pb is one of major ecological concern because of its high potential to accumulate in individual organisms and in the entire food chain. Table 2 shows the concentration of total Pb in the soil profile at sites A, B and C. The total Pb concentration varied from 59 (180- to 240-cm depth) to 758 μ g/g dry weight (0- to 90-cm depth). The highest Pb concentration observed at 0- to 90-cm depth was at site B, whereas the lowest at the same soil depth

TABLE 1.—*Physico-chemical characteristics of JBNERR sediments.*

Site id	K	Ca	Mg	Na	OM
	meq/100g				%
A	1.55 b ¹	21.01 b	9.97 a	3.34 b	0.73 b
B	0.54 b	28.91 a	9.23 a	3.12 b	5.09 a
C	3.44 a	26.21 ab	9.63 a	22.88 a	2.59 ab

¹Within columns, means followed by the same letter are not significantly different at P < 0.05.

TABLE 2.—Lead concentrations in samples of soil from sites A, B and C (see Figure 1).

Depth (cm)	Site A Pb ($\mu\text{g/g}$)		Site B Pb ($\mu\text{g/g}$)		Site C Pb ($\mu\text{g/g}$)	
	Total	HCl	Total	HCl	Total	HCl
0 to 90	63 a ¹	9.40 a	758 a	6.00 a	132 a	3.77 b
90 to 180	61 a	3.03 b	89 b	6.63 a	65 b	4.47 a
180 to 240	59 a	2.95 b	65 b	3.55 a	63 b	4.25 ab

¹Within columns, means followed by the same letter are not significantly different at $P < 0.05$.

was at site A. Lead concentration decreased with soil depth at sites B and C, but not at site A. Acid-extractable Pb was significantly lower than the total Pb; and from 0 to 90 cm, the concentration significantly increased as follows: site A > site B > site C (Table 2). The high concentrations of the total Pb in topsoil northeast of JBNERR, the decreasing trend of total Pb with soil depth at sites B and C, and the lack of Pb in the rock weathering process of soil formation (Seguinot, 2001) indicate anthropogenic activities as the main Pb sources. Lead accumulates in northeast of JBNERR possibly because of the proximity to urban development and other industrial and waste facilities.

In order to evaluate Pb movement in the JBNERR soils, the partition coefficient was determined. The partition coefficient was the ratio of heavy metal bound to soil ($\mu\text{g/g}$) versus heavy metal ion in aqueous phase ($\mu\text{g/mL}$). Partition of Pb was studied by adding increasing amounts of Pb^{+2} to JBNERR soil slurries. Lead was not detected in the aqueous phases after one hour of contact since JBNERR soils are capable of trapping Pb^{+2} very fast. The JBNERR soils are high in organic matter, CaCO_3 and CaHCO_3 contents, all of which explains their rapid sorption of Pb^{+2} (Strawn and Sparks, 2000; McBride et al., 2000). Correlation of added Pb with dissolved Ca indicates very rapid substitution of Ca with Pb or a rapid formation of Pb compounds with releasing of Ca (Figure 2A).

Table 3 shows the effect on Pb availability after equilibration of JBNERR soil with four concentrations of saline water for seven days ($\text{pH} = 7.4$). Only a small fraction of the Pb is in aqueous solution at 0%, in comparison with that of the other treatments, which indicates an enhanced dissolution or exchange of Pb (higher partition coefficient) with salinity (Fig. 2B). Laing et al. (2008) reported a similar effect of salinity on the partition coefficient of Cd. The addition of Pb^{+2} to the soil slurry at the same salinity level did not affect the amount of available Pb after reaching equilibration. The above finding indicates that JBNERR soil has very high capacity to sorb Pb. Enhancement of Pb remobilization from soil because of competition of cations such as Ca, Mg and Na for

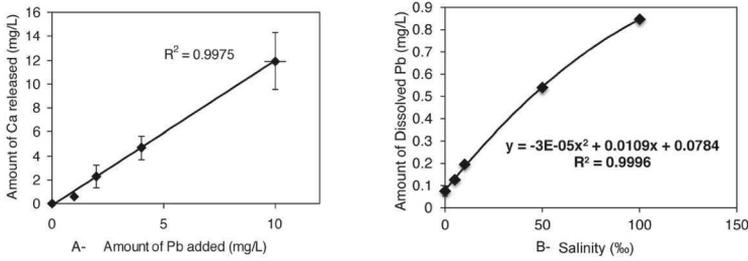


FIGURE 2. Relation between the amount of Ca released and the amount of added Pb (A), and the remobilization of Pb from JBNERR sediment with the increase of artificial seawater salinity (B).

sorption sites has been reported (Tsai et al., 2003). In addition, the rate of Pb remobilization from soil could also be affected by the high concentration of phosphate, chloride, and organic matter (McLean and Bledsoe, 1992; Dong et al., 2000), which are common in tidal flooded-affected areas.

Nutrients and heavy metals in interstitial water

Groundwater in JBNERR is alkaline, anoxic, and salty. The average pH, electric conductivity, major cations (Na^+ , K^+ , Ca^{+2} , Mg^{+2}) and levels of phosphate and ammonia nutrients in groundwater samples are shown in Table 4. Transect I, closer to the northern boundary of JBNERR, had the lowest range of EC in interstitial water (7544 $\mu S/cm$). The mean EC for interstitial water in transect IV, closer to the southern black mangrove dieback area, was 146,719 $\mu S/cm$.

Concentrations of Na, K and Mg in groundwater samples followed the above-mentioned electrical conductivity pattern (Table 4), which indicates seawater as a major source of these nutrients (Table 1). Table

TABLE 3.—Effect of salinity on the Pb dissolution from JBNERR duplicate soil samples.

Salinity (‰)	0	5	10	50
added Pb (mg/L)	Pb (mg/L)			
0	0.06	0.13	0.19	0.54
0	0.09	0.13	0.20	0.54
1	0.18	0.08	0.15	0.50
1	0.18	0.04	0.15	0.48
2	0.01	0.11	0.13	0.45
2	0.01	0.08	0.16	0.45
10	0.02	0.12	0.15	0.48
10	0.05	0.07	0.14	0.50

TABLE 4.—Annual mean concentrations of some groundwater quality properties, groundwater from piezometers one to five in transects I to IV, June 2004 to May 2005.

Transect id	pH	EC μ S/cm	Na mg/L	K	Ca	Mg	N-NH ₃	N-NO ₃	P-PO ₄
I	8.05 a	7,544 d ¹	1,142 d	6 d	116 c	149 d	1.33 b	0.24 a	0.19 b
II	7.66 b	34,634 c	4,767 c	166 c	618 b	923 c	7.66 a	0.10 a	1.18 b
III	7.57 b	73,679 b	9,807 b	276 b	959 a	1,852 b	4.06 ab	0.15 a	1.47 b
IV	7.69 b	146,719 a	21,127 a	735 a	1,014 a	3,069 a	4.55 ab	0.11 a	10.28 a

¹Within columns, means followed by the same letter are not significantly different at P < 0.05.

4 shows that interstitial water pH from JBNERR is alkaline, which is related to the high amount of calcium bicarbonate from mineral dissolution (Rodríguez, 2006). The interstitial water pH decreased with the conductivity, which indicates the mixing of the fresh alkaline water from the aquifer with seawater.

Table 5 shows that the mean concentrations of Pb in the interstitial water decreased in the order that follows: transect IV > III > II > I. Figure 3 shows a lineal correlation of annual soluble Pb concentration with annual EC, an indication that marine water enhanced Pb remobilization in JBNERR's sediment, or that seawater had Pb.

Piezometers in transect IV were located in a black mangrove dieback area. The black mangrove dieback area was very close to agricultural lands, which explains the higher concentration of PO_4^{-3} in the above-mentioned piezometers. Phosphate anion promotes dissociation of natural organic matter from aluminum and iron oxide minerals (Kaiser and Zech, 1999). The natural organic matter promotes the formation of Pb-natural organic matter complexes, which could increase dissolution of Pb from mineral surfaces (Town and Filella, 2002).

Piezometers in transect IV were in a tidal-affected area, which induce reducing condition in this area. In reducing conditions, Mn^{+4} is reduced to Mn^{+2} (Hseu and Chen., 1999; Mitsch and Gosselink, 1986).

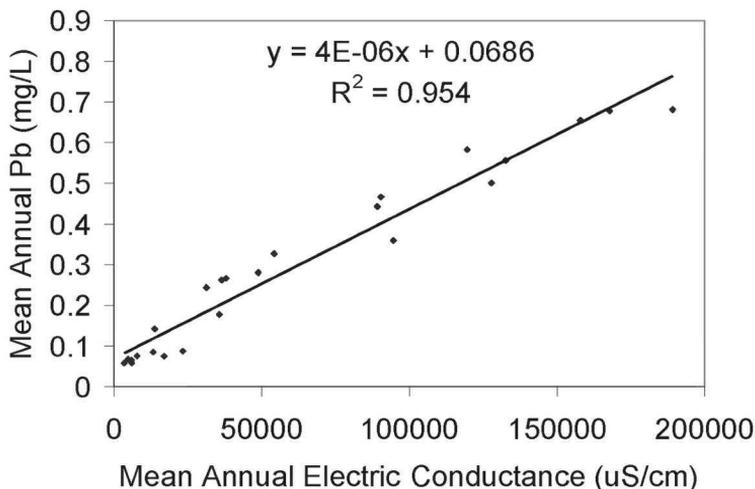


FIGURE 3. Linear regression between mean annual soluble lead concentrations and mean annual electric conductivity of groundwater samples in the study area.

TABLE 5.—Annual average concentrations and standard deviations of Pb, Cr and Mn in groundwater from transects I to VI, June 2004 to May 2005.

Transect	Pb	Cr	Mn
	mg/L		
I	0.0048 d ¹	0.01 d	0.44 b
II	0.16 c	0.16 a	3.09 a
III	0.27 b	0.03 c	3.14 a
IV	0.56 a	0.10 b	4.70 a

¹Within columns, means followed by the same letter are not significantly different at P < 0.05.

The reducing conditions in JBNERR that promote the formation of reduced Mn species are related to the trend in concentration of Mn in the interstitial water in the study area.

Interstitial waters in transect II had the highest Cr concentration; because the piezometers were along a former agricultural drainage canal, they were probably affected the most by anthropogenic activities as compared to the other transects. The reductive (anoxic) conditions of the tidal-affected area on JBNERR must promote the sink of Cr, which explains both non-detection of Cr in the interstitial water and the retention of Cr (III) species in the drainage canal, and also explains why no further spread of Cr was found (McLean and Bledsoe, 1992).

Organic compounds in interstitial water

Organic compounds, such as benzothiazole (< 10 ppb), were found in the JBNERR interstitial water. These compounds are indicators of the potential impact anthropogenic activities, which occur close to JBNERR, have on the ecosystem quality. Benzothiazole is an organic compound that has been associated with tire manufacturing, disposal and industrial wastewater (Evans et al., 2000). In addition, traces of 1-methyl-2-pyrrolidinone, an industrial solvent, tert-butyl phenol and some plasticizers were detected. It is important to remark that no residues of agricultural pesticides used on nearby farms were found, a fact which indicates the low impact of pesticides on the study area of JBNERR.

CONCLUSION

The increase in salinity decreases the partition coefficient of Pb from JBNERR soil. Correlation of Pb sorption and remobilization of Ca indicates the higher binding strength of Pb compared to Ca by sediment surfaces. The amount of Pb in JBNERR was higher than acute and chronic levels as indicated in the NRWQC for salt water (0.21 and 0.008 mg/L, respectively). Thus, the above data suggests that the near anthropogenic sources are major contributors of Pb pollution in JB-

NERR. Chromium seems to be immobilized by intrinsic anoxic conditions of JBNERR in a former agricultural drainage canal, thus no further problems with Cr are expected in this area. Higher concentrations of Mn in black mangrove dieback area confirm that reductive conditions promote its remobilization. The trend of heavy metals from estuary-flooded soils towards nursery and the open sea need to be studied to mitigate further damages in the JBNERR ecosystem.

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