

# An assessment of metal contamination in mangrove sediments and leaves from Punta Mala Bay, Pacific Panama

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## Abstract

Due to the growing rate of urbanisation in many tropical coastal areas, there continues to be an increasing concern in relation to the impact of anthropogenic activities on mangrove forests. Punta Mala Bay is located on the Pacific coast of Panama and suffers from intense anthropogenic activities that are potentially harmful to the remaining mangrove forests. Field observations reveal that the mangrove stand within Punta Mala Bay receives high inputs of untreated domestic sewage, storm water run-off and a range of diffuse inputs from shipping activities. Results from analysis of eight metals (Mn, Cu, Zn, Ni, Pb, Fe, Cr, Cd) showed that Fe, Zn and Pb were in concentrations high enough to conclude moderate to serious contamination within the bay, and thus pose the most threat to the regeneration and growth of the mangrove. However, previous biological surveys indicate ongoing mangrove regeneration and domination of stand structure by *Laguncularia racemosa*, together with high numbers of seedlings and saplings.

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## 1. Introduction

Elevated concentrations of heavy metals have been recorded in mangrove sediments all over the world, which often reflects the long-term pollution caused by human activities (Lacerda et al., 1992; Perdomo et al., 1998; Harris and Santos, 2000; Tam and Wong, 2000). Heavy metals are amongst the most serious pollutants within the natural environment due to their toxicity, persistence and bioaccumulation problems (MacFarlane and Burchett, 2000). Due to their inherent physical and chemical properties, mangrove muds have an extraordinary capacity to accumulate materials discharged to the near shore marine environment (Harbison, 1986). Mangrove sediments are anaerobic and reduced, as well as being rich

in sulphide and organic matter. They therefore favour the retention of water-borne heavy metals (Silva et al., 1990; Tam and Wong, 2000) and the subsequent oxidation of sulphides between tides allows metal mobilisation and bioavailability (Clark et al., 1998). Concentrations of heavy metals in sediments usually exceed those of the overlying water by 3–5 orders of magnitude (Zabetoglu et al., 2002) and, with such high concentrations, the bioavailability of even a minute fraction of the total sediment metal content assumes considerable importance with respect to bioaccumulation within both animal and plant species living in the mangrove environment. Since heavy metals cannot be degraded biologically, they are transferred and concentrated into plant tissues from soils and pose long-term damaging effects on plants.

Many mangrove ecosystems are close to urban development areas (Tam and Wong, 2000; MacFarlane, 2002; Preda and Cox, 2002) and are impacted by urban and industrial run-off, which contains trace and heavy metals in the dissolved or particulate form. The Republic

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of Panama lost 41% of its mangrove cover between 1960 and 1988, with the majority of loss on the Pacific coast (Ellison and Farnsworth, 1996). Punta Mala Bay is a small, semi-tidal coastal bay located on the Pacific coast of Panama. The vegetation of the bay is one of the few remaining mangrove forests in the city area. Since 1999 there have been ongoing construction activities near this mangrove. The construction of a dual carriageway, shopping complexes and mass land reclamation in the past five years suggests that disturbance and pollution input within the area is high and likely to increase. Field observations reveal that the mangrove stand within Punta Mala Bay receives high inputs of heavy metals from untreated domestic sewage, storm water road run-off and diffuse inputs from shipping and agricultural activities (Guzman and Jimenez, 1992). Approximately  $7 \times 10^7$  tonnes of oil is annually transported through the Panama canal (D'Croz, 1993) suggesting that petroleum, as well as ballast waters, will continue to be a potential pollutant impacting the mangroves within Punta Mala Bay, which is located in close proximity to the Pacific entrance of the canal. *L. racemosa* or 'white mangrove' is dominant in Punta Mala Bay (Benfield, 2002). This species is known to flourish in contaminated areas (Tomlinson, 1999) so their abundance within the mangrove stand within Punta Mala Bay initially suggests that the area could be experiencing a pollution disturbance.

The aim of this study was twofold: to provide a preliminary study to determine current levels of eight commonly polluting metals: manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), iron (Fe), chromium (Cr) and cadmium (Cd); and to determine the degree of spatial variation of metals in sediments and leaf within the study area.

## 2. Materials and methods

### 2.1. Area of investigation

A survey was conducted in May 2003 at Bahía Punta Mala, a small bay located adjacent to Panama City, Pacific Panama. This south-facing bay is approximately 400 m wide and 1 km in length (8°56'N and 79°33'W). Vegetation studies were carried out in May 2003 on five previously assessed monitoring plots (Benfield, 2002). Each plot measured 10 m × 10 m and methods were followed as described by English et al. (1997) and Benfield (2002).

### 2.2. Sediment and leaf collection and analyses

Three replicate sediment samples from the upper 5 cm of sediment over an area of approximately 5 cm × 5 cm were randomly collected from each plot using a clean, acid-washed plastic scoop. Samples were

stored in clean acid-washed plastic containers until transportation to the laboratory. Individual sediment samples were wet sieved through a 1 mm bronze mesh with distilled deionised water and collected in a clean, labelled, acid-washed glass jar. The samples were left in a closed running fume cupboard for approximately one week. Samples were then oven dried at  $60 \text{ °C} \pm 5 \text{ °C}$  for 24 h to eliminate any remaining water content. Samples were homogenised and stored in a dry acid-washed plastic bag for metal analysis.

Twenty leaves from 5–10 *L. racemosa* trees were collected from within each of the five plots. Leaves were collected from trees that were greater than 1 m tall with a girth at breast height of greater than 2.5 cm and that were of similar health condition (as determined by degree of predation on leaves). However, tree leaves damaged by predation were not always avoidable. Leaves were subsampled ( $n = 3$ ), washed in distilled water, oven dried at  $60 \text{ °C}$  for 24 h and homogenised (methods adapted from studies performed by MacFarlane et al., 2003).

All samples of sediment and dried leaves were transported back to the UK in clean (acid-washed) sealed plastic sample bags. Samples were analysed in a clean and uncontaminated fume cupboard on arrival in the UK. Oven dried and homogenised sediment samples (1.0 g) and *L. racemosa* leaf tissue (1.0 g) were used for analysis. Samples were digested for heavy metal analysis with a  $90 \text{ °C}$  mixture of concentrated nitric acid and hydrogen peroxide, after the method by Krishnamurty et al. (1976) and MacFarlane et al. (2003), and made to 25 ml volume. Digested samples were stored in labelled, acid-washed glass vials. Metal analysis was carried out immediately on the resultant digests using air/acetylene atomic absorption spectroscopy (AAS), with the use of prepared standards (run before each batch) to determine sample concentrations. To ensure precision of AAS results, three replicates of each sample were run to ensure measured absorbencies were consistent. Metal concentrations were calculated from each replicate absorbance value, which was then used to calculate an average sample metal concentration. For sediment samples, eight metals were analysed using AAS: Mn, Zn, Cu, Pb, Fe, Ni, Cr and Cd. Only three metals within leaf tissue were of interest in this study: Cu, Zn and Pb were analysed since these metals can be used as bioindicators of heavy metal exposure (MacFarlane, 2002). Metal concentration in ppm ( $\mu\text{g/ml}$ ) was determined for each sample and an average calculated from the three replicates. The absorbance of a blank sample was also conducted to allow background correction.

### 2.3. Metal statistical analysis

The mean and standard error of determined metal concentrations within samples were calculated. Differences among metal concentrations in sediments and

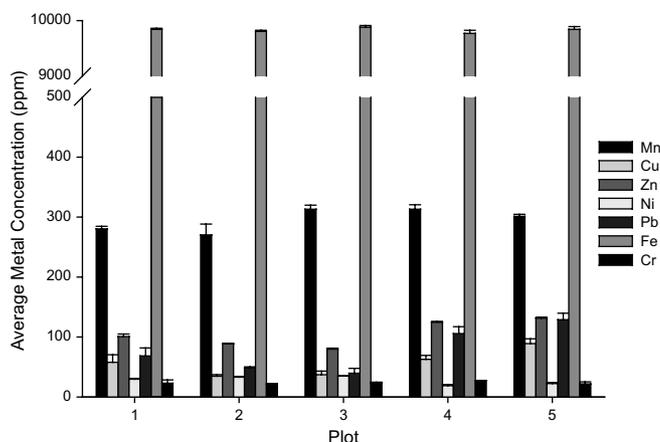


Fig. 1. Average concentration (ppm dry wt + SE) of iron, manganese, zinc, copper, lead, nickel and chromium in sediment (<1 mm fraction) from plots 1–5 in Punta Mala Bay, Panama, measured using AAS.

leaves from different plots were tested using One-Way ANOVA. Statistically significant differences between groups were assessed using Tukey's multiple comparison test.

### 3. Results

#### 3.1. Sediment metal levels

Iron had the highest mean value (9827 ppm), followed by manganese (295 ppm), zinc (105 ppm), lead (78.2 ppm), copper (56.3 ppm), nickel (27.3 ppm), chromium (23.3 ppm) and cadmium (<10 ppm) (Fig. 1, Table 1). Concentrations of Fe (One-Way ANOVA,  $df = 5, 17; F = 1.15; P > 0.1$ ), Mn ( $df = 5, 17; F = 2.36; P > 0.1$ ), and Cr ( $df = 5, 17; F = 2.88; P > 0.05$ ) were not significantly different between monitored plots. Concentrations of Zn ( $df = 5, 17; F = 28.4; P < 0.05$ ), Cu ( $df = 5, 17; F = 7.28; P < 0.05$ ), Ni ( $df = 5, 17; F = 29.02; P < 0.05$ ) and Pb ( $df = 5, 17; F = 5.41; P < 0.01$ ) were found to be significantly different between monitored plots over the mangrove area.

#### 3.2. Leaf metal levels

Copper measured in leaf tissue ranged from 2.27 to 5.00 ppm dry wt. Average [Cu] was 3.73 ppm dry wt (Table 1). Significant differences between leaf concentrations in monitored plots were observed (One-Way ANOVA:  $df = 4, 14; F = 9.68; P < 0.05$ ). Zinc concentrations measured within leaf tissue ranged from 33.4 to 41.4 ppm dry wt. Significant differences between leaf concentrations in monitored plots were observed (One-Way ANOVA:  $df = 4, 14; F = 37.31; P < 0.05$ ). Lead concentrations measured within leaf tissue ranged from 2.66 to 9.32 ppm dry wt and differences were significant between

plots (One-Way ANOVA;  $df = 4, 14; F = 52.45; P < 0.01$ ). Average leaf Pb level was measured at 6.13 ppm (Table 1).

### 4. Discussion

The concentrations of all metals analysed in the sediments in Punta Mala Bay are comparable with concentrations of metals found in other tropical areas receiving industrial pollution (Table 1). Iron had the highest mean value (9827 ppm), followed by manganese (296 ppm), zinc (105 ppm), lead (78.2 ppm), copper (56.3 ppm), nickel (27.3 ppm), chromium (23.3 ppm) and cadmium (<10 ppm). This trend follows a distinctly similar pattern (Fe > Zn > Pb > Ni > Cu > Cr > Cd) in mangrove sediments from an area under intense development and industrialisation in Hong Kong (Ong Che, 1999). According to background values from the Hong Kong Environment Protection Department (Tam and Wong, 2000), concentrations of Fe, Zn and Pb measured in Punta Mala Bay can be considered to present a high level of contamination and a serious threat to the mangrove ecosystem. Cu currently presents a moderate to serious threat, whilst Ni can be considered to be causing slight contamination in the bay. At the time of this study, Cr and Cd appear to present no hazard to the mangrove system, with concentrations being measured in the region of expected natural background levels.

Sediment concentrations of Zn, Cu, Ni and Pb were found to be significantly different between monitored plots over the mangrove area, whilst concentrations of Fe, Mn and Cr were not. Given the restricted geographical coverage of this study of an isolated mangrove community within a small bay it is difficult to read too much into the significance of these differences but some

Table 1

Comparison of sediment and leaf metal levels (ppm dry wt) between Punta Mala Bay, Panama and other documented sediment levels (ppm dry wt) from around the world

Location	Mn	Zn	Cu	Pb	Ni	Cr	Fe	Cd
Panama	Sediment							
Punta Mala Bay	295	105	56.3	78.2	27.3	23.3	9827	<10
Toro Point <sup>a</sup>	294	19.9	4.9	38	82.4	13.7	1885	6.6
Galeta <sup>a</sup>	143	10.9	4.0	32.5	74	12.8	1748	7.2
Payardi <sup>a</sup>	228	16.1	4.0	33.3	91.8	10	2094	7.5
Costa Rica								
Punta Portete <sup>a</sup>	268	14.7	8.4	34.5	102	22.6	3225	7.3
Punta Piuta <sup>a</sup>	525	11.4	9.8	25.6	99.0	19.8	6118	6.0
Colombia								
Cienaga Grande <sup>b</sup>	623	91.0	23.3	12.6	32.5	13.2	15593	1.92
Australia								
Port Jackson <sup>c</sup>	–	145	62.0	180	–	–	–	–
Port Jackson <sup>c</sup>	–	351	102	443	–	–	–	–
Hawksbury <sup>c</sup>	–	94	18.9	26.4	–	–	–	–
Port Hacking <sup>c</sup>	–	10.3	1.1	2.5	–	–	–	–
Queensland <sup>d</sup>	103	23–56	1–12	36	9.0	1–72	1056	0.6
Brazil								
Clean Mangrove <sup>e</sup>	–	24.2	3.82	–	–	–	2464	0.6
Hong Kong								
Clean mangrove <sup>f</sup>	96	43	2.6	31.2	2.9	1.2	1.08% <i>dw</i>	0.32
Panama	Leaves							
Punta Mala Bay (L)	–	35.8	3.7	6.2	–	–	–	–
Australia								
Port Jackson (Site 1) (A) <sup>c</sup>	–	22.1	24.8	3.5	–	–	–	–
Port Jackson (Site 2) (A) <sup>c</sup>	–	35.5	10.7	3.9	–	–	–	–
Hawksbury (A) <sup>c</sup>	–	14.3	3.2	1.7	–	–	–	–
Port Hacking (A) <sup>c</sup>	–	34.0	3.2	0.1	–	–	–	–

Documented 'clean' mangrove sites are noted in italics.

Australian mangrove in Port Hacking was deemed a clean and unpolluted mangrove, situated within a National Marine Park. Hawksbury and Port Jackson (Sites 1 and 2), Australia were reported to be polluted mangroves with regard to metal pollution. (A) = *Avicennia marina* (from MacFarlane, 2002), (L) = *Laguncularia racemosa*.

<sup>a</sup> Guzman and Jimenez, 1992.

<sup>b</sup> Perdomo et al., 1998.

<sup>c</sup> MacFarlane, 2002.

<sup>d</sup> Preda and Cox, 2002.

<sup>e</sup> Harris and Santos, 2000.

<sup>f</sup> Tam and Wong, 2000.

variation may be attributed to effects of biological and physical phenomena, such as tidal inundation, salinity changes, wind and waves. These phenomena allow the processes of bioturbation, re-suspension and erosion that are known to affect the metal concentrations in surface sediments (Bellucci et al., 2002). The unvegetated zones in Punta Mala Bay were characterised by highly reducing, algal covered black mud. Marcomini et al. (1993) confirmed that surficial concentrations of some metals could be strongly influenced by the development of a redox condition in mangrove sediments and that covering of the sediment by an algal mat could influence the settlement of metals out of water.

Copper measured in leaf tissue between plots ranged from 2.27 to 5.00 ppm dry wt. Average leaf Cu concentration was 3.73 ppm dry wt (Table 1). Average leaf Zn

concentration was 35.8 ppm (range 33.4–41.4 ppm) with very little variation between plots. These levels correspond with concentrations measured from *Avicennia* sp. growing within unpolluted mangroves in Australia where copper was measured at 3.20 ppm dry wt (MacFarlane, 2002). In a heavily polluted mangrove MacFarlane (2002) measured leaf Zn at 14.3 ppm and 34.0 ppm in an unpolluted mangrove situated in a National Marine Park. Average leaf Pb concentration in Punta Mala Bay was measured at 6.14 ppm (range 2.7–9.3 ppm), higher than any documented levels by MacFarlane (2002). It is difficult to relate these differences in the reported values for *Avicennia marina* and *L. racemosa* as variations are likely to be due to physiological differences and the variations that exist in accumulation strategies of different plant species. However, elevated

concentrations of non-essential metals in tissues do suggest a possible function of sequestering toxic metals, especially with respect to lead (Ong Che, 1999). MacFarlane et al. (2003) reported that significant relationships between *A. marina* leaf tissue and sediment did occur, but were weak and were not maintained temporally. The recorded leaf Pb levels in this study could present a future concern as non-essential metals often become toxic at low concentrations (MacFarlane and Burchett, 2001). Further studies of the mangroves in Punta Mala Bay and nearby sites would have to be conducted to investigate whether or not similar processes occurred in *L. racemosa*.

However, a number of researchers have previously measured high concentrations of accumulated metals in the tissues of mangrove species, with no apparent impact on plant health (Gleason et al., 1979; Clough et al., 1983; Perdomo et al., 1998; MacFarlane and Burchett, 2001, 2002; MacFarlane et al., 2003). This appears to be the case in Punta Mala Bay, where vegetation analysis in previous studies (Benfield, 2002) shows that regeneration and growth of this *L. racemosa* is, at the present time, highly successful and does not appear to be inhibited by contamination. Large numbers of seedlings and established saplings were observed in the study area and appeared to be flourishing in measurements taken and compared between the 2002 and 2003 seasons. *L. racemosa* is reported to pioneer readily in disturbed sites where it can form pure stands (Tomlinson, 1999) and self-fertilising individuals have also been reported that would aid them in being a successful pioneering species. The success of *L. racemosa* in this bay is most likely due to the plant's ability to actively avoid the uptake of metals, even when sediment concentrations are high. Mechanisms of plant tolerance to heavy metals are thought to include cell wall immobilisation, sequestering (Baker and Walker, 1990), barriers at root epidermis, exclusion of ions (Walsh et al., 1979; Baker and Walker, 1990) and peroxidase induction (Dietz et al., 1999). However, Wong et al. (1988) reported that when plants absorbed and accumulated heavy metals, the vessels became constricted and deposits of an unknown substance blocked the vascular system and retarded the water transportation. Yim and Tam (1999), provided evidence from a mangrove wastewater loading study (containing Cu, Zn, Cd, Cr and Ni at concentrations of 30, 50, 2.0, 20 and 30 mg l<sup>-1</sup> respectively), that high heavy metal concentrations significantly reduced leaf number and stem basal diameter in *Bruguiera gymnorhiza* after just 63 days of wastewater treatment. Old leaves were seen to turn yellow and shed off whilst young leaves continued to survive.

The majority of studies show few significant correlations between metal levels in sediment and metals in tissues, which suggests that mangroves actively avoid metal uptake and/or most metals are present below the

sediment bioavailability threshold (MacFarlane et al., 2003). This study found sediment metals in concentrations significantly above expected natural background levels and in some cases reaching levels that might be classified as highly contaminated (Tam and Wong, 2000). Yim and Tam (1999) found that, in general, very small amounts of heavy metals were accumulated in leaf tissues as most absorbed heavy metals were accumulated in stem and root tissue. MacFarlane (2002), MacFarlane and Burchett (2002) and MacFarlane et al. (2003) indicate that root tissue has more potential as an environmental bioindicator than leaves. It is suggested that any further investigations within the *L. racemosa* population of Punta Mala Bay should include root metal level measurements as an aid to future management and, that for a better understanding of metal uptake, sampling should extend to other areas within the region to obtain a greater variety and extremes of environmental contamination levels.

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