

Metal Sorption Capabilities of Two Common Plants in Tropical Wetlands - *Bambusa vulgaris* and *Raffia bambusa**

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Abstract

In most developing countries, careless disposal of waste dry cell batteries and Ni-Cd batteries from mobile phones and rechargeable lamps has led to an increase in some metal contaminants including copper, lead, nickel and cadmium in soils and water bodies. These metals have the potential to cause serious, and sometimes, irreversible health effects if they are consumed. Unfortunately, in most cases, either the water bodies are not treated prior to consumption or the water treatment methods do not target the removal of these metals. This study therefore sought to mimic the bio-filtering effect of wetlands by assessing the capabilities of two common plants in tropical wetlands; *Raffia bambusa* and *Bambusa vulgaris* to remove Cu^{2+} , Pb^{2+} , Ni^{2+} and Cd^{2+} from wastewater. Spectroscopic characterisation indicated that some of the functional groups on the biomass were the OH, C=O and COOH, and *R. bambusa* appeared to have more pronounced groups than *B. vulgaris*. The results show maximum sorption of 95% Cu and Pb by biomass derived from roots of these plants. Sorption of Cd and Ni were lower at about 40%. By using a 3-stage sorption system of live plants, sorption of Cd and Ni increased up to 80%.

Keywords: Heavy Metals, Sorption, Biomass, *Bambusa vulgaris*, *Raffia bambusa*

1 Introduction

The increase in metal ion concentration in the environment due to technological advancement has been an issue of major concern (Ehrlich and Brierley, 1990; Volesky, 1990; Glazer and Nikaïdo, 1995; Volesky and Holan, 1995; Ehrlich, 1997; Tsezos, 2001; Volesky, 2001; Amankwah and Yen, 2005). Toxic/heavy metal-contaminated waste may be generated from anthropogenic activities such as mining, smelting, electroplating and manufacturing operations among others. Another major source is improper recycling of electronic waste (e-waste).

In a study conducted by Anon (2010), e-waste was found to be the fastest growing component of municipal waste, with the total annual global volume approaching 40 million metric tonnes. E-waste generally contains substantial amounts of heavy/toxic metals including lead, cadmium, nickel, chromium, copper, mercury and arsenic (Man *et al.*, 2013). Waste recycling methods such as burning, melting, chopping and acid digestion may lead to release of a wide range of toxic chemicals which add to the concentration of heavy metals in the environment (Terazono *et al.*, 2006).

Ghana, like most developing countries, is gradually becoming a dumping ground for e-waste, and Agbogbloshie market in Accra has become a major site for recycling such waste (Asante *et al.*, 2012; Oteng-Ababio, 2012; Itai *et al.*, 2014; Oteng-Ababio *et al.*, 2014). Studies by these researchers

show that metals and metalloids associated with e-waste such as lead, mercury, arsenic, cadmium, selenium, chromium and copper are accumulating in soils, water bodies and even in the tissues of workers who recycle such materials. In Ghana, since domestic/municipal wastewater is generally not treated, these metals when solubilised may be transported from the point of generation and affect communities downstream.

Another scenario that increases the metal ion concentration in the environment is careless disposal of metal components due to less stringent environmental enforcement of recycling methods. For example, the problem of unreliable power supply from national grids has resulted in increasing usage of battery-powered lamps in households and offices. In addition, there is a geometric increase in the use of mobile phones (Kochi, 2012; Fortin, 2013). These units are mostly powered by Ni-Cd rechargeable batteries and dry cells, and careless disposal of these batteries has led to an increase in the presence of lead, nickel and cadmium in surface and ground waters (Volesky, 2001). The solubility and mobility of these metals, and possible accumulation and retention throughout the food chain, leads to serious ecological and health hazards to both flora and fauna (Gupta and Ali, 2004; Iyer *et al.*, 2005; Bayo *et al.*, 2009; Ibrahim, 2011; Areco *et al.*, 2012).

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There is thus an urgent need to process wastewaters before discharge into the general environment. In addition, remediation of contaminated water bodies should also be investigated. Available technologies include ion exchange, reverse osmosis, electrochemical reduction, membrane technology, chemical precipitation, adsorption on activated carbon, solvent extraction and biosorption (Volesky and Holan, 1995; Volesky, 2001; Davis *et al.*, 2003; Bayo *et al.*, 2009).

Biosorption focuses on the metal binding capacities of various plants and lower animals. In recent times, biosorption has become a preferred method for metal decontamination, especially when dealing with contaminants of dilute solutions. This is because it presents a technically simple and economically viable alternative to the abiotic processes (Glazer and Nikaido, 1995; Volesky and Holan, 1995; Hawari and Mulligan, 2006; Ahluwalia and Goyal, 2007; Fu and Wang, 2011).

Biosorption may be accomplished in natural systems or by the use of treated biomass. In the natural environment, wetlands play a dominant role. Wetlands act as biofilters, and combines phytoremediation with microbial activity (Park *et al.*, 2011). They also serve as a cheaper alternative to chemical processes in metal immobilisation (Yong *et al.*, 2006).

Preliminary studies in some parts of Ghana by the authors showed a consistent increase in the concentration of nickel, cadmium, lead and copper in water bodies, partly due to careless disposal of waste batteries and other electronic wastes (Asamoah *et al.*, 2012). If not checked, this development has the potential to pollute both surface and ground waters and also affect biotic organisms. The increase in concentrations of these metal ions is especially pronounced in small-scale gold mining environments where the miners use these batteries to power lamps for night duties and underground operations. In such areas, also, land disturbance exposes sulphide minerals which undergo oxidation leading to acid generation and reduction of the pH of some surface waters to between 5 and 6. These acidic waters enhance solubilisation of metals from the waste electronic components after they have been discharged indiscriminately in the environment.

Unfortunately, normal pipe-borne water treatment procedures may not target these metals, and in some cases, the water may not even be treated before domestic consumption. It is therefore imperative to source treatment methods that are technically simple, economically viable, readily available, and environmentally friendly.

Surface waters usually encounter plants as they flow in their courses and/or pass through wetlands.

Some plants such as *Bambusa vulgaris* and *Raffia bambusa* are common in tropical wetlands, and may contribute to the removal of dissolved metals. However, the metal sorption capabilities of these plants are yet to be documented. This paper therefore sought to mimic the metal-filtering ability of wetlands by using the roots of *B. vulgaris* and *R. bambusa* as biosorbents for the sequestration of Cd, Pb, Ni and Cu. The aim was to ascertain if such plants can be incorporated into contaminated water bodies to enhance natural purification before the water is used domestically, especially in areas where there is no pipe-borne water.

2 Resources and Methods Used

2.1 Materials

The roots of *B. vulgaris* and *R. bambusa* (Fig. 1) were harvested from wetlands in south-western Ghana. In the first approach, the roots were washed thoroughly with de-ionized water, air-dried, and then cut to sizes between 4.0 and 2.0 mm. The dry weight of the biomass was determined after drying at 70°C. In the second approach, live plants were used after washing to get rid of soil. Artificial wastewater containing multiple metal ions; Cd, Pb, Ni and Cu with concentrations, 10 ppm, 50 ppm, 100 ppm was prepared by dissolving appropriate quantities of cadmium chloride, lead nitrate, nickel sulphate and copper sulphate respectively in distilled water.



Fig. 1 *Raffia bambusa* (a) and *Bambusa vulgaris* (b)

2.2 Methods

2.2.1 Biomass-Metal Ion Interactions

The roots of *B. vulgaris* and *R. bambusa* were brought into contact with 250 ml of artificial wastewater in 500-ml Erlenmeyer flasks, and the flasks were agitated at a low rate of 80 rpm using an MRC incubator shaker for up to 180 minutes at 25°C. Three biomass concentrations of 0.1, 0.5 and 1.0 g/L were prepared to examine the effect of biomass concentration on biosorption. After an adsorption cycle of up to 180 minutes, the biomass was separated by filtration, and the metal ion concentration in the aqueous phase was determined using Varian AA240FS Atomic Absorption Spectrometer.

Following investigations with dry chips, further experiments with live plants were also conducted. A 3-stage sorption system was set up with 3 vases and wastewater was contacted with live biomass. The wastewater was allowed to flow from one stage to the other (Fig. 2), and the solution samples exiting each stage after the expected retention time were analysed. The solution was allowed to flow through by gravity at a flow rate of 20 ml/min to ensure good contact between biomass and wastewater. The flow rate allowed a retention time of 6 h per stage and 21.6 L of wastewater was treated altogether. The wet mass of the plants was $500 \text{ g} \pm 20 \text{ g}$.

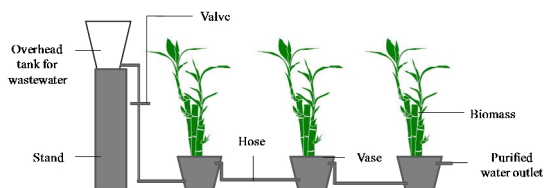


Fig. 2 Set-up for 3-stage Process (Sketch of Bamboo Obtained by Courtesy of Openclipart.org)

In all experiments, the pH was kept at 5.4 ± 0.2 by the addition of dilute nitric acid or sodium hydroxide. This is because biosorption is affected by changes in pH due to changes in the dissociation of functional groups present on the surface of the biomass. At low pH values, there is excessive protonation of the active sites and hence competition between hydrogen ions and other metal ions for the same sites leading to a reduction in sorption rate. In addition, metal ion precipitation may also occur at pH values above 6.0 (Fourest and Roux, 1992; Fourest and Volesky, 1996).

2.2.2 Fourier Transform-Infrared Spectroscopy of Biomass

The functional groups on the dry biomass were determined by Fourier transform infrared analysis using a Bomem Gramps/32 Spectrometer. Pulverised biomass was mixed with KBr in a ratio of 1:150 and the spectra were recorded between 700 and 4000 cm^{-1} . The axes of each spectra were normalised to facilitate comparison.

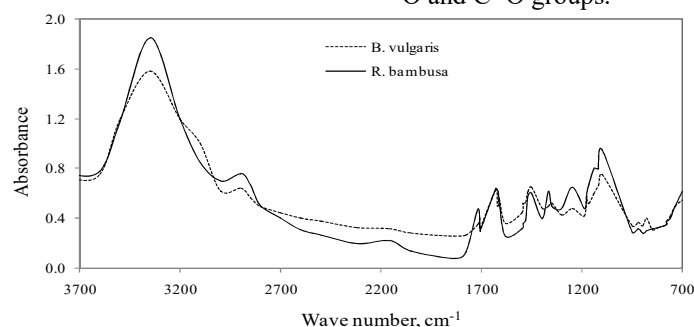


Fig. 3 Infrared Spectrograph of *R. bambusa* and *B. vulgaris*

2.2.3 Calculation of Percent Metal Removal and Root Sorption Capacity

At the end of the biosorption experiments, the residual metal ion concentration C_e and the initial metal ion concentration C_o were utilised in estimating the metal sorbed by the biomass, R (Equation 1).

$$R = \left(\frac{C_o - C_e}{C_o} \right) \times 100\% \quad (1)$$

The sorption capacity, q (mg of metal/g of biomass), of the biosorbents was determined using Equation 2:

$$q = V(C_o - C_e)/W \quad (2)$$

where V is the volume of solution (L) and W is dry weight of biomass (g).

3 Results and Discussion

3.1 Spectroscopic Characterisation of Biomass

Some studies using biomass for sorption of toxic/heavy metals attribute sequestration to the presence of functional groups on the biomass that interact with the metal ions. Thus the spectrographic characterisation was done to identify such groups. The spectrographs of both biomasses are shown in Fig. 3. The peak assignments are based on data provided by Faix (1992) and Boeriu *et al* (2004).

The peak between 3350 and 3320 cm^{-1} is from the presence of OH groups and generally attributed to the presence of water. Boeriu *et al* (2004) also ascribed the OH groups to phenolic and aliphatic structures associated with lignin. The bands centered around 2900 , 1620 and 1460 cm^{-1} are predominantly for CH_2 and CH_3 , and that at 1100 cm^{-1} is due to the COOH group. Other peaks were detected at $1705 - 1720 \text{ cm}^{-1}$ which are associated with the C=O group. Boeriu *et al* (2004) attributed the band at $1370-1375$ to phenolic (OH) and aliphatic C-H in methyl groups and the peak assignment at 1220 cm^{-1} can be ascribed to C-C, C-O and C=O groups.

It can be seen that both biomass showed similar spectra. However the absorbance at some wave numbers such as between 3350 and 3320 and around 2900, 1220-1250 and 1100 cm^{-1} were higher for *R. bambusa* than for *B. vulgaris*. Thus it could be deduced that *R. bambusa* had more pronounced C=O, COOH, CH₂ and CH₃ groups.

3.2 Wastewater - Dry Biomass Interactions

Fig. 4 shows the sorption curve for copper when the wastewater was contacted with both *R. bambusa* and *B. vulgaris* at various biomass concentrations. For all biomass concentrations, *R. bambusa* proved to be a better adsorber than *B. vulgaris*. From an initial copper ion concentration of 100 ppm, 0.1 g/L *R. bambusa* reduced the copper concentration by 55% within 15 minutes, 70% after 60 minutes, and 85% after 180 minutes. In a similar manner, 1.0 g/L *R. bambusa* reduced copper ion concentration by 70% after 15 minutes and 91% after 180 minutes. This indicates that the metal ion has been sequestered, possibly by some surface functional groups such as the carbonyl, and carboxylic acids on the biomass (Fig. 3).

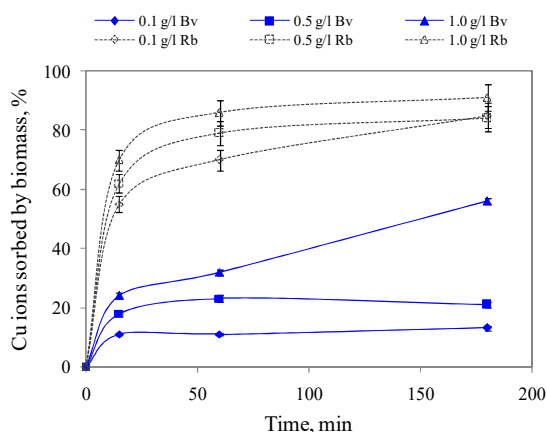


Fig. 4 Sorption of Cu on *B. vulgaris* (Bv) and *R. bambusa* (Rb) at various Biomass Concentrations. Initial Cu Concentration was 100 ppm

For 0.1 g/L and 0.5 g/L *B. vulgaris*, the residual copper ion values were quite high at 87 ppm and 80 ppm respectively after 180 mins. The residual concentration, however, reduced with increased biomass concentration; for 1.0 g/L *B. vulgaris*, as the residual copper ion concentration was 44 ppm, showing that more than 50% was sorbed. For *R. bambusa*, however, more than 80% of the metal ion was sorbed at all biomass concentrations.

The sorption curves for Pb ions were quite different from those for Cu as both *R. bambusa* and *B. vulgaris* sorbed higher concentrations of Pb, above 65% (Fig. 5). From an initial Pb concentration of 100 ppm, sorption was very high within the initial 15 minutes and continued at a much slower rate until 180 minutes. With *R. bambusa*, final sorption values

were above 90% at all biomass concentrations, with 1.0 g/L achieving 99.5% metal sorption. Similar biosorption curves with a sharp initial sorption rate followed by a slow section have been reported in the literature (Volesky, 1994; Volesky and Holan, 1995; Chen and Yiaccaumi, 1997).

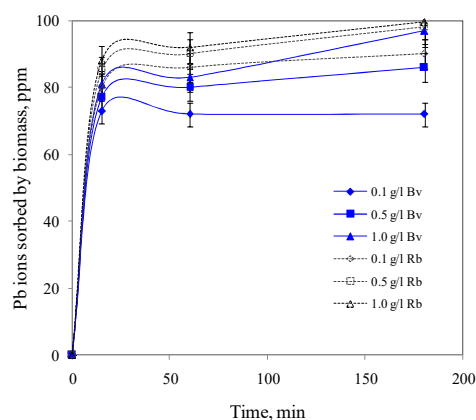


Fig. 5 Sorption of Pb on *B. vulgaris* (Bv) and *R. bambusa* (Rb) at various Biomass Concentrations. Initial Pb Concentration was 100 ppm

Fig. 6 compares sorption of Cu and Pb by both biomass types from solutions of initial metal ion concentration of 10 ppm and 0.1 g/L biomass. The trend showed that most of the metal was sorbed quickly within the initial 15 minutes followed by a slow sorption process until 180 minutes. All samples showed some degree of metal ion reduction after the test period with a maximum of 90% for Pb using *R. bambusa* as sorbent. It is thus clear that when the initial metal ion concentration is lower, percentage sorption is higher.

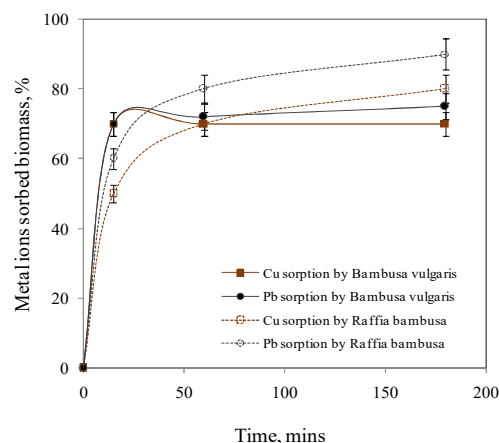


Fig. 6 Comparative Study of Sorption of Cu and Pb using 0.1 g/L Concentrations of *B. vulgaris* and *R. bambusa*. Initial Concentration of Cu and Pb was 10 ppm

Fig. 7 shows that sorption of Cd and Ni by *B. vulgaris* was relatively low at 30% and 20% respectively after 15 minutes, and increased slightly

to about 38% and 45% after 30 minutes. Beyond this period, the metal ions were desorbed into solution, and after 180 minutes, sorption was between 20 and 30% in both cases. This observation may be due to saturation of the active sites on the biomass. *R. bambusa* sorbed higher concentrations within the initial 15 minutes, and the curve shows desorption and re-adsorption of metal ions over the processing period, ending at about 45% sorption after 180 min. Figs. 4-7 demonstrate that the two biomass types utilised have higher affinity for Pb and Cu than for Cd and Ni.

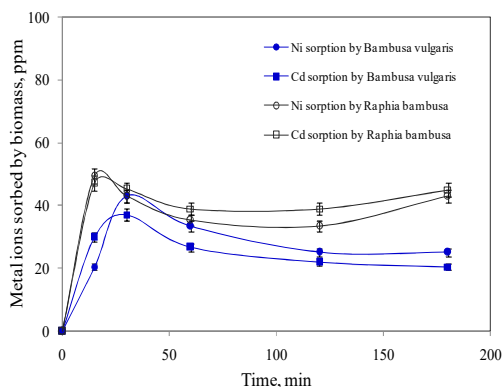


Fig. 7 Sorption of Ni and Cd by *B. vulgaris* (Bv) and *R. bambusa* (Rb). Initial Metal Ion and Biomass Concentrations were 100 ppm and 1.0 g/L Respectively

3.3 Sorption capacity

Figure 8 shows a plot of sorption capacity against initial metal ion concentration. The sorption capacities generally increased with increasing initial metal ion concentration. Taking the sorption of Pb by *B. vulgaris*, for example, as the initial Pb concentration was raised from 10 ppm through 50 ppm to 100 ppm, the sorption capacity increased from 2.5 through 12.4 to 24.3 mg of metal per gram of biomass. A similar trend was obtained for Cu.

The sorption capacities of Ni and Cd onto *B. vulgaris* were quite low with a maximum value of 5 mg/g at initial solution concentration of 100 ppm. For all the metal ions, sorption onto *R. bambusa* was higher by 3 - 40%. The higher sorption capacity of *R. bambusa* may be attributed to the marked C=O and COOH groups that are known to interact with and sequester metal ions (Volesky and Holan, 1995; Volesky, 2001).

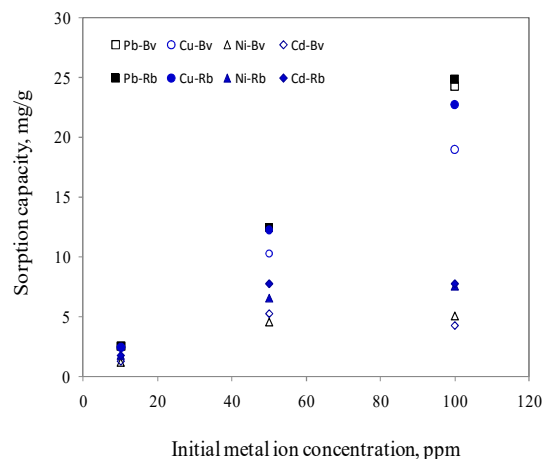


Fig. 8 Sorption Capacities of Pb, Cu, Ni and Cd by *B. vulgaris* (Bv) and *R. bambusa* (Rb)

In the literature, many researchers have attributed sorption preferences to the functional groups on the biomass to the charge and size of the ions being sorbed (Volesky, 1994; 2001). In this study, variations in the amount of metal sorbed may not be attributed to charge as all the metals have a charge of +2. Cu^{2+} and Ni^{2+} ions are smaller than those of Pb^{2+} and Cd^{2+} , thus size also did not play a dominant role.

3.4 Sorption with Live Plants

Following sorption studies with chips of dry biomass, further investigations were conducted using live biomass. Fig. 9, which illustrates the sorption profile, shows that there was a consistent reduction in metal ion concentration from one stage to the next. This may be attributed to contact between wastewater and fresh biomass with more active sorption sites. For Cu and Pb, there were sharp drops in concentration in the initial stage, and there was further reduction till the concentration dropped below 0.05 ppm by the end of the third stage. There was a reduction in the concentration of Ni and Cd in all three stages as the wastewater came into contact with fresh biomass. From an initial concentration of 100 ppm, the final metal ion concentrations in solution were between 15 and 25 ppm for *R. bambusa* and 50 to 55 ppm for *B. vulgaris*. In a real life situation, the biomass will accumulate these metals, which will become toxic to the plants over time.

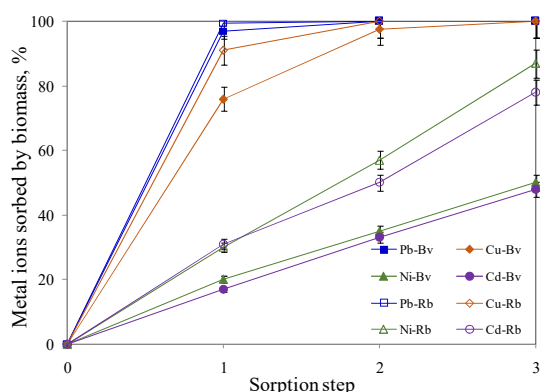


Fig. 9 Three-stage Sorption of Pb, Cu, Ni and Cd by Live Plants of *B. vulgaris* and *R. bambusa*. Initial Metal Ion and Biomass Concentrations were 100 ppm and 500 g Respectively

Comparing the mass of dry biomass against the volume of solution it came into contact with, the dry biomass sorbed more metal ions per unit weight of biomass than the live version. However, for applications on metal ion sequestration in natural environments, live biomass may be much easier to apply.

Sorption of metal ions by these plants may have public health implications. Juice from *R. bambusa* is tapped and drunk locally as palm wine but *B. vulgaris* is not used for food. Further studies are required to know the part of the *R. bambusa* tree where these metal ions are stored and whether there is the potential for the metal ions to contaminate the palm wine produced. There is ongoing work to using real wastewater which contains other components to evaluate the performance of the biosorbents.

4 Conclusions

This study was conducted to investigate the sorption of cadmium, lead, copper and nickel using *B. vulgaris* and *R. bambusa*. Some of the functional groups on the biomass were the OH, C=O and COOH and *R. bambusa* appeared to have more pronounced groups than *B. vulgaris*. These functional groups interact with and sequester the metal ions.

The variables tested were contact time, biomass concentration and initial metal ion concentration. The metal ion concentration tested was in the range 10 to 100 ppm. From the study, it can be concluded that both materials have the potential to sorb the metal ions considered, with the highest removal efficiency and affinity towards lead. Maximum sorption values of over 95% Cu and Pb were achieved by biomass derived from roots of *B. vulgaris* and *R. bambusa*. Sorption of Cd and Ni were lower at about 40%.

The 3-stage sorption process helped to achieve 99.5% sorption of Cu and Pb using both biomasses. For Cd and Ni, 50% sorption was achieved with *B. vulgaris* and about 80% with *R. bambusa*. In all cases *R. bambusa* showed higher sorption capacities than *B. vulgaris* and this may be attributed to the more prominent functional groups which are known to interact with and capture metal ions. These plants may thus be grown extensively in areas where inhabitants do not have access to pipe-borne water, and surface waters containing these metal ions are used for drinking. In the long-term, the best strategy is to toughen up the pollution prevention measures and apply catchment management techniques to prevent metal pollution of water bodies.

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