12

Arsenic accumulation by aquatic and terrestrial plants

Taupo Volcanic Zone, New Zealand

Brett Robinson, Monica Marchetti, Christophe Moni, Lina Schroeter, Carlo van den Dijssel, Georgie Milne, Nanthi Bolan & Santiago Mahimairaja

Introduction

The Taupo Volcanic Zone (TVZ) covers an area of 600 000 ha in the central North Island, New Zealand. It extends from White Island south-west to Mount Ruapehu in a long narrow belt. The area features five active volcanoes that include White Island, Mt Tarawera, Mt Tongariro, Mt Ngauruhoe and Mt Ruapehu. The area is rich in hydrothermal activity, abounding in hot springs, geysers and mud pools. Such areas occur in specific fields of geothermal activity. The TVZ contains over 32 natural lakes, including Lake Taupo (the largest lake in New Zealand) and Lake Rotorua. New Zealand's longest river, the Waikato, flows out of Lake Taupo through several geothermal fields and north-west to the Tasman Sea. Seven hydroelectric power dams have been built along this river to exploit the 366 m fall to the sea (Liddle 1982).

Geothermal activity in the TVZ has resulted in elevated arsenic (As) concentrations in some lakes and rivers (Aggett & Aspell 1978). The As loading in surface waters is exacerbated by the commercial exploitation of geothermal power (Axtmann 1975). Historically, As has also been introduced into the aquatic environment from runoff of As-based pesticides (Hill 1975), aquatic pesticides used to control lake weed (Tanner & Clayton 1990) and leaching from timber-treatment sites that used copper-chromium-arsenic (CCA) biocides.

The predominant form of As in the environment is arsenate (As^{V}) since arsenite (As^{III}) is oxidized by atmospheric oxygen (Pepper et al. 1987). For most of the year, over 90% of the As in the Waikato River, which flows through the TVZ, is present as As^{V} (Aggett & Aspell 1978) but in the summer months the levels of As^{III} increase, probably because of microbial reduction (Freeman 1985).

It is widely known that some aquatic macrophytes growing in the TVZ and Waikato River contain high concentrations of As (Reay 1972; Liddle 1982). Robinson et al. (1995a) reported >1000 mg/kg^{-1} (ppm) As (dry weight) in samples of *Egeria densa* and *Ceratophyllum demersum* growing in the Waikato River system.

Liddle (1982) conducted experiments involving the uptake of As by *Ceratophyllum demersum*. He found that plants grown in As solutions with <0.1 mg/L^{-1} As (^{III} or ^{V}) reached equilibrium in one or two days, while plants in >0.5 mg/L^{-1} of this element needed up to a week to reach equilibrium. Arsenic concentration in plants increased with increasing concentration of As in

the growing medium. At a similar As concentration in the growing medium, plants grown under laboratory conditions contained far less As than plants collected under natural conditions in the Waikato River.

A survey of watercress (*Lepidium sativum*) growing in the region revealed concentrations as high as 1766 mg/kg^{-1} in the shoot (Robinson et al. 2003). This is of concern to human health because watercress is consumed as a vegetable. On a fresh-weight basis, nearly all the samples tested were above 2 mg/kg^{-1}, the World Health Organization (WHO) limit for As in foodstuffs (Brandsetter et al. 2001). Plant-accumulation of As may also facilitate the entry of this toxic element into the food chain.

Arsenic uptake by plants is associated with the phosphate ion ($H_2PO_4^-$) uptake mechanism, where presumably As^V is taken up as a $H_2PO_4^-$ analog (Khattak et al. 1991; Meharg & Macnair 1991; Pickering et al. 2000). Ma et al. (2001) reported As concentrations in the Brake fern, *Pteris vittata*, of up to 22 000 mg/kg^{-1} (2.2%) on a dry-matter basis. This is the first terrestrial species reported to take-up As to concentrations greater than 1000 mg/kg^{-1}, the threshold for a plant to be considered a hyperaccumulator (Brooks et al. 1977). It has been shown that aquatic plants accumulate trace elements by absorption followed by passive or active transport across membranes (Forstner & Wittmann 1981; Smies 1983).

Hyperaccumulator plants could be used for the phytoremediation of As-contaminated sites (Ma et al. 2001). This technology relies on plants that translocate inordinate amounts of one or more metal(loid)s including As into their above-ground biomass. Arsenic phytoremediation would involve repeated cropping until the soil's As concentration reached an acceptable level. After each cropping, the plant biomass would be removed from the area and may be burned to reduce its volume, whereupon it could be stored in an appropriate area, such as a contained landfill, that does not pose a risk to the environment. The possibility of using hyperaccumulator plants to extract As from aquatic environments has also been suggested (Brooks & Robinson 1998). This chapter presents the As uptake by terrestrial vegetation adjacent to geothermal areas where soils may have elevated As concentrations, following a survey of the As uptake by aquatic macrophytes in the TVZ. Data obtained under controlled conditions on the As uptake of five fern species that are known to occur in the TVZ are also presented.

Materials and methods

Field surveys

A number of terrestrial and aquatic plant samples were taken at several sites along the Waikato River and around geothermal areas in the TVZ. Leaf samples were collected from the terrestrial plants, while whole specimens of the aquatic plants were taken. Aquatic samples were washed in river water to remove sediment, then further washing in distilled water was carried out upon returning to the laboratory. Samples were stored in paper bags for drying.

Greenhouse experiments

The greenhouse experiment was performed at Hort Research, Palmerston North, New Zealand (40.2°S, 175.4°E). Five species of native ferns (*Asplenium bulbiferum*, *Blechnum discolor*, *Histiopteris incisa*, *Pneumatopteris penningera* and *Polystichum vestitum*) as well as watercress (*Lepidium sativum*) were grown in 15 L buckets containing soils spiked with sodium arsenate to give final As concentrations of 0, 55 and 105 mg/kg^{-1}. There were five replicates for each treatment. The soil used was Manawatu silt loam, with a pH of 4.4 and a total organic matter content of 6.3%. Soils were prepared by adding varying amounts of a 1% As solution to c. 15 kg of soil and mixed using a concrete mixer. Soils were fertilized with Nitrosol^{TM} liquid fertilizer

at a rate recommended by the manufacturer. Planting occurred at the end of October 2002, some six weeks after preparation of the soil samples. This delay was to allow time for the added As to come to equilibrium with the soil. Plants were watered at least once every two days, depending on evaporative demand. Pots were arranged in a randomized block design within the shadehouse. Plant samples were taken for chemical analysis in mid-January 2003, 10 weeks after planting.

Sample preparation and As determination

Plant material, sediments and soils were placed in a drying cabinet at 80°C until a constant weight was reached. Plant material was ground using a mortar and pestle. Sediment and soil samples were sieved to <1 mm size using a nylon sieve and stored in sealed plastic bags.

Approximately 0.15 g of ground plant material or 0.5 g of sieved sediment and soil sample was accurately weighed into 50 mL Erlenmeyer flasks. 10 mL of concentrated nitric acid (69%) were added to each flask and the mixtures heated and evaporated on a heating block until a final volume of c. 3 mL was reached. The samples were then diluted to 10 mL using distilled water and stored in polythene containers.

All samples of plant material, sediment and waters were analyzed for As using graphite furnace atomic absorption spectroscopy. Due to the high concentrations of As being measured in some of the plant samples, plant standards were unavailable. Thus, for quality assurance, 14 dried and ground plant samples were sent to a commercial laboratory (Hill Laboratories, Hamilton, New Zealand) for comparison. The results were in good agreement ($R^2 = 0.978$), but our results were consistently 5–30% higher than those of the commercial laboratory, possibly due to differences in the digestion methods.

Statistical treatment of data

MINITAB was used for ANOVA and correlation analyses. For data that were log-normally distributed, we report geometric means and standard deviation ranges rather than means and standard deviations.

Results and discussion

Arsenic accumulation in terrestrial and aquatic plants from the TVZ

The average As concentrations in the soils, sediments and waters, as well as aquatic and terrestrial plants collected from the TVZ during the field survey, are presented in Tables 12.1 and 12.2. The geometric mean As concentration in the water samples was over twice that of the New Zealand and WHO Drinking Water Standard (0.01 mg/L^{-1}) and significantly higher than that recorded in countries where As poisoning has been reported (see Chapters xx–xx). There was a clear demarcation between terrestrial plants, that accumulated negligible concentrations of As, and aquatic species that had As concentrations many-fold higher than the ambient waters whence they were taken.

The As concentrations in aquatic and terrestrial species from the Waikato River and TVZ are given in Tables 12.2 and 12.3 respectively. The data clearly display the difference in As accumulation between aquatic and terrestrial plants. All aquatic plants accumulated measurable As concentrations with many species exceeding the threshold concentration of 1000 mg/kg^{-1} (on a dry-matter basis) for hyperaccumulation (Brooks et al. 1977). By contrast, 83% of the terrestrial plants (Table 12.3) were below the detection limit for As (<0.5 mg/kg^{-1}). All the aquatic plants tested accumulated As to concentrations greater than 5 mg/kg^{-1} on a dry-matter basis, and none of the terrestrial plants tested had As concentrations surpassing 11 mg/kg^{-1}.

Table 12.1 Arsenic accumulation in aquatic species collected from the. Plant concentrations are in mg/kg^{-1} (dm = dry matter, fm = fresh matter); water concentrations are in mg/L^{-1}. Where more than one sample was collected (denoted by the number in brackets), the average concentration is reported.

Location	Water [As]	Species	[As] dm	[As] fm	B.C.[a]
Tokaanu geothermal region and upper Waikato River					
Tokaanu	0.091	*Callitriche petriei* (3)	4278	272	47130
		Ceratophyllum demersum	765	34.5	8424
		Elodea canadensis (3)	1442	52	15889
		Lagarosiphon major (2)	666	nd	nd
		Lemma minor	808	24	8901
		Mentha piperata (5)	600	49	6608
		Myriophyllum propinquum (9)	2960	152	32603
		Polygonum hydropiper (4)	763	56	8411
		Rorippa nasturtium-aquaticum (19)	1628	69	17936
		Veronica aquatica (2)	625	51	6887
Aratiatia	0.007	*Ceratophyllum demersum*	142	nd	19789
		Egeria densa	131	nd	18363
		Lagarosiphon major	286	nd	39898
Ohaaki	0.014	*Ceratophyllum demersum* (3)	550	nd	40749
		Egeria densa	2908	202	215404
		Lagarosiphon major	85	nd	6348
		Lemma minor (3)	171	18	12683
		Rorippa nasturtium-aquaticum (3)	145	5.6	10711
		Mentha piperata	91	10	6734
		Myosotis laxa	64	3	4758
		Polygonum salicifolium	71	4	5228
		Rumex crispus	4	0.5	294
		Veronica aquatica (2)	47	1	3638
Mihi	0.035	Algae	191	21	12509
		Alisma plantago	29	5	838
		Callitriche petriei	489	45	13943
		Ceratophyllum demersum (2)	572	19	16304
		Cyperus ustulatus	21	6	585
		Egeria densa	1318	70	37562
		Glyceria maxima	1.3	0.2	37
		Lagarosiphon major (2)	568	59	16180
		Nymphaea alba	12	1	351
		Polygonum hydropiper (2)	126	8	3600
		Polygonum salicifolium	39	3	1118
		Veronica aquatica	25	1	721

Location	Water [As]	Species	[As] dm	[As] fm	B.C.[a]
Lower Waikato River					
Ohakure	0.022	*Callitriche petriei*	365	46	16549
		Ceratophyllum demersum	904	22	41024
		Egeria densa	892	nd	40492
		Juncus sp. (2)	18	3	811
		Glyceria maxima	28	3	1291
		Rorippa nasturtium-aquaticum (10)	186	9	8415
		Mentha piperata	7	1	328
		Nymphaea alba (3)	35	2	1573
		Potamogeton orchreatus	110	8	4980
		Veronica aquatica (3)	6	0.2	277
Whakamaru	0.039	*Egeria densa*	728	48	18293
		Lagarosiphon major	643	48	16623
Maraetai	0.065	*Callitriche petriei*	618	199	9483
		Ceratophyllum demersum	263	13	4037
		Glyceria maxima (2)	22	6	342
		Juncus sp. (2)	25	6	376
		Nymphaea alba (2)	11	0.8	172
Waipapa	0.029	*Ceratophyllum demersum*	366	16	12693
		Egeria densa	854	42	29663
Karapiro	0.039	*Ceratophyllum demersum* (3)	292	13	7219
Huntly	0.029	*Ceratophyllum demersum* (2)	86	4	2930
		Egeria densa	158	9	5407
		Glyceria maxima	28	4	964
Tuakau	0.031	*Cyperus eragrostis* (4)	70	13	2290
		Egeria densa	116	8	3787
		Juncus spp. (2)	26	5	856
		Lycopus europaeus (2)	103	16	3353
		Polygonum hydropiper	27	4	870
Port Waikato	nd (saline)	*Ceratophyllum demersum*	99	nd	nd
		Cyperus eragrostis	24	5	nd
		Juncus spp. (4)	20	nd	nd

[a] bioaccumulation coefficient
nd = not determined

Outridge and Noller (1991) noted the difference in metal(loid) accumulation between aquatic and terrestrial species in their review of hyperaccumulation of elements by freshwater plants. Although they did not provide an explanation of this phenomenon, various reasons could be attributed for the difference in As accumulation between aquatic and terrestrial plants. In terrestrial systems, solubilization of As in the rhizosphere may be necessary to allow the plant roots to take up this element. An efficient As transport and storage system needs to

Table 12.2 Arsenic accumulation in aquatic species collected from the TVZ. Plant concentrations are in mg/kg^{-1} dry matter, water concentrations are in mg/L^{-1}

Species	No. of samples	% dry matter	Plant GeoMean (As) and SD range	Water GeoMean (As)	GeoMean BC[a]
Hot-water algae[b]	3	3	3019 (1058–8617)	0.32	9345
Cold-water algae[b]	10	8.5	36.7 (7.3–184.9)	0.03	1452
Alisma plantago aquatica	2	10.2	40.3 (25.8–63.1)	0.02	1853
Callitriche stagnalis	3	6.4	4215 (3402–5223)	0.09	49 307
Callitriche petriei	2	11.0	422 (343–520)	0.03	15 190
Ceratophyllum demersum[b]	16	6.9	284 (119–769)	0.03	10 606
Convolvulus arvensis	1	10.9	17.0	0.03	580
Cyperus eragrostis	5	17.8	47.5 (21–105)	0.05	1049
Cyperus ustulatus	1	28.7	20.5	0.04	584.9
Egeria densia[b]	8	6.1	568 (189–1701)	0.02	24 847
Elodea candensis[b]	6	6.2	68 (2.5–1837)	0.01	4987
Glyceria maxima	5	17.6	13.9 (3.7–52.5)	0.04	352
Juncus spp.	14	24.5	9.8 (2.4–39.4)	0.08	116
Lagarosyphon major[b]	11	7.8	127 (7.7–2107)	0.02	8502
Lemma minor[b]	9	2.9	15 (0.6–360)	0.01	1793
Lepidium sativum	33	4.6	369 (58.7–2325)	0.04	9174
Lotus corniculatus	2	10.7	637 (344–1179)	-	-
Lycopus europaeus	2	15.9	102 (91–114)	0.03	3343
Mentha piperata/ var. citrata	4	9.1	167 (14.8–1884)	0.04	4361
Mentha spicata	3	9.9	181 (88.7–370.4)	0.13	1361
Myosotis laxa	1	4.7	64.2	0.01	4758
Myriophyllum propinquum[b]	10	4.7	2101 (873–5056)	0.08	27 860
Nymphaea alba	6	8.0	16.5 (7.5–36.4)	0.03	483
Polygonum hydropiper	8	8.1	114 (19.3–672)	0.05	2423
Polygonum salicifolium	4	7.4	44 (10.0–197.8)	0.01	3126
Potamogeton orchreatus	5	7.3	144.6 (26.5–808)	0.01	16 188
Rumex crispus	1	11.5	3.9	0.01	294
Rumex obtusipholius	1	24.1	97.3	0.04	2274
Typha orientalis	3	9.5	174 (113–267)	0.09	2042
Veronica aquatica	5	3.8	10.0 (3.4–29.0)	0.02	459

a: Bioaccumulation coefficient

b: Species that lack extensive root systems

exist for accumulation to occur in the aerial parts. This is not the case when the plant grows in an aqueous medium, where the metalliod is already present in bioavailable form and can be absorbed and/or adsorbed by the leaves.

Table 12.3 Arsenic concentrations (mg/kg^{-1} dry matter) in terrestrial species collected from TVZ

Name	No. of samples	Minimum (no. of samples below detection limit)	Maximum
Asplenium polyodon	1		<0.5
Blechnum capense	5	<0.5 (3)	1.2
Cyathodes juniperina	1		<0.5
Dicranopteris linearis	1		<0.5
Histiopteris incisia	6	<0.5 (5)	1.4
Juncus sp.	2	<0.5	1.4
Kunzea ericoides	5		<0.5
Leptospermum scoparium	6	<0.5 (5)	11
Lycopodium cernuum	1		<0.5
Paesia scaberula	3	<0.5 (2)	0.6
Pittosporum tenuifolium	1		<0.5
Pteridium esculentum	4		<0.5

Sixteen different species of aquatic plants were tested and all of them accumulated higher concentrations of As than the terrestrial plants. Algae growing in the water of Tokaanu had the highest concentration of As (1252–9632 mg/kg^{-1} dry matter). Specimens of numerous other species were found to accumulate more than 1000 mg/kg^{-1} As. Most specimens of *Myriophyllum propinquum* (geomean 2101, sd range 873–5056 mg/kg^{-1}) were over the 1000 mg/kg^{-1} threshold. There have been no previous reports of As hyperaccumulation by this species.

Previous studies of As uptake by aquatic plants from the TVZ (Liddle 1982; Robinson et al. 1995b; Brooks & Robinson 1998; Robinson et al. 2003) focused on four species: *Ceratophyllum demersum*, *Egeria densa*, *Lagarosiphon major* and *Lepidium sativum*. These studies reported average As concentrations in *C. demersum, E. densa*, *L. major* and *R. nasturtium* of 400, 500, 300 and 400 mg/kg^{-1} respectively. Although sampled at different locations, the results in this study were in good agreement, being 284, 568, 127 and 369 mg/kg^{-1} respectively.

The present study also determined As levels in several species that had not previously been analyzed. It was found that *M. propinquum*, *E. canadensis* and hot-water algae from Tokaanu all accumulated As to levels greater than 1000 mg/kg^{-1}. Additionally, *Callitriche petrei*, *Lotus corniculatus*, *Lycoptus europaeus*, *Mentha* spp., *Polygonium hydropiper*, *Potamogeton orchreatus* and *Typha orientalis* all accumulated more than 100 mg/kg^{-1}. Although not technically hyperaccumulators, As accumulation by these species may be environmentally significant because they represent a food source for animals and, in the case of *Mentha* spp., for humans.

Arsenic accumulation in ferns and watercress from As-spiked soil

The ferns and watercress grew well in all the treatments of As-spiked soils and there were no signs of As toxicity. None of the fern species or the watercress had foliar As concentrations greater than 0.5 mg/kg^{-1} dry matter (the detection limit for As), even at the highest soil As concentration of 105 mg/kg^{-1}. There were no significant differences in the soil As concentration before and after the experiment, indicating that leaching losses were insignificant.

None of the ferns tested has potential for As phytoremediation because they failed to accumulate significant amounts of As from the soil.

Watercress, a plant that grows in both the aquatic and terrestrial environment, accumulated As only when grown in the former. This implies that watercress is not efficient in absorbing As through roots in the sediments and/or has no specialized mechanism for translocating

As to the above-ground tissues. It also raises the question of whether As is absorbed or adsorbed from the aquatic system. Arsenic may simply bind to the cell surfaces of aquatic plants, indicating that there is no specialized As-uptake mechanism. However, in such a scenario the plants would still need to have a tolerance mechanism for As.

The low plant uptake in the greenhouse experiment may be explained by low As bioavailability in the soil. Arsenic bioavailability in soils is a key factor for its uptake by plants. Even if the total As concentrations in the soils were high, it is possible that the element was strongly bound to the soil particles and thus relatively unavailable for plant uptake. The relatively acid soil pH (measured at 4.4 in this experiment) that ferns favor (Metcalf 1993) may render As less available than at higher pHs (Manning & Goldberg 1997; Smith et al. 1999; Tyler & Olsson 2001; Raven et al. 1998). Arsenic bioavailability may be further reduced by As binding to clay particles and organic matter in the soil. Soil factors influencing As bioavailability are discussed in detail in Chapter 15.

When comparing the results from this experiment with those of Ma et al. (2001), who showed *Pteris vittata* could hyperaccumulate As from a soil containing less As than the highest treatment in this trial, it is clear that either the ferns tested in this experiment have no specialized As-uptake mechanism or that the bioavailability of As varied between the soils. The As hyperaccumulator *Pteris vittata* has the ability to solubilize As in the root zone, then translocate it to the aerial tissues. This mechanism must overcome the relatively low bioavailability of As in the soil.

Arsenic bioaccumulation coefficient

The concentration of As in the plant alone may not necessarily explain its efficiency in extracting the element from soil or water, because the substrate As concentration partially determines plant uptake. It is therefore necessary to compare the concentration of As in the plant in relation to the concentration found in the environment in which the plant is growing. Logically, a plant growing in a medium rich in (bioavailable or total) As would be expected to contain a higher amount of that element in its tissues. However, in phytoremediation, an important trait of the plants is their ability to extract As even if it is present in low concentrations in the substrate.

The bioaccumulation coefficient is defined as the ratio of the concentration of As in the plant and the concentration of As in the growing medium (Brooks & Robinson 1998):

$$\text{Bioaccumulation coefficient} = \frac{[\text{As}]\text{plant}}{[\text{As}]\text{environment}}$$

where As concentration in plant = mg/kg^{-1} dm, As concentration in soil = mg/kg^{-1} soil and As concentration in water = mg/L^{-1}.

The geometric means of the bioaccumulation coefficients for the plants tested in this experiment are shown in Table 12.2. The results presented here show only the plant/water bioaccumulation coefficient. Some of the aquatic plants tested were rooted to sediments that had an As concentration many times the level of the water, but still less than the plant concentration. The ability to take up As was not affected by whether the plant is rooted or free-floating, with three of the seven free-floating species having bioaccumulation coefficients higher than 10 000.

The bioaccumulation coefficients for the aquatic plants in this study are higher than any previously reported for terrestrial species, but are comparable to those calculated using previous studies on aquatic plants (Reay 1972; Liddle 1982; Robinson et al. 1995a, 2003). The ranking of the bioaccumulation coefficients is different from the results for the total As concentration in the plants. Studies on terrestrial plants have shown that bioaccumulation coeffi-

cients tend to decrease as the ambient concentration increases (Robinson et al. 2000), although in soil this may be a function of metal bioavailability as well as plant uptake.

Bioindication of As contamination by aquatic plants

The high bioaccumulation coefficients of some aquatic species may make them good candidates for the bioindication of As contamination in aquatic systems. A bioindicator is an organism or a set of organisms whose biological response towards different environmental factors gives information about the present condition and/or evolution of an ecosystem.

In the case of aquatic plants, the pertinent biological response to As contamination is high bioaccumulation coefficient. The potential value of using aquatic macrophytes as bioindicators is that they provide information on the history of As in the water, rather than a snapshot at the time of sampling. Arsenic levels in water vary depending on dilution caused by rainfall, concentration caused by evaporation or sporadic contamination (e.g. accidental chemical spill) and volatilization caused by biomethylation. Furthermore, analyzing aquatic macrophytes may elucidate any historic As contamination even if current levels in water are within acceptable limits. Plants collected near Blenheim, South Island, New Zealand, exemplify the use of aquatic macrophytes in this role. Analysis of water samples collected from Pukaka Stream and Spring Creek showed As concentrations lower than the detection limit of 0.05 mg/L^{-1}, although Pukaka Stream has been reported to have As concentrations up to 0.08 mg/L^{-1} during low-flow times. Analysis of *E. canadensis* collected in Pukaka Stream showed an average As concentration of 2.5 mg/kg^{-1} on a dry-matter basis, a result that indicates the presence of elevated As levels in the water, if not at the time of sampling then certainly in the past. *E. canadensis* taken from Spring Creek, a stream with no known As contamination, had <0.5 mg/kg^{-1} As, indicating the absence of significant quantities of As.

Generally, bioindicators should be easily identified, abundant and widely distributed (for a better comparison between different sites); a large size, limited mobility and a long lifecycle are other important characteristics. Aquatic macrophytes such as the hornwort (*Ceratophyllum demersum*) fit all these criteria, with the possible exception of mobility. This plant is free-floating and may migrate downstream in times of flood.

Arsenic concentration data for *Ceratophyllum demersum* and ambient water from a previous study (Robinson et al. 1995a) was reprocessed to illustrate the relationship between plant As concentration and that of the ambient water (Figure 12.3). There was a highly significant correlation ($r^2 = 0.70$, $P < 0.001$), indicating that the As concentration of the plants could be used to predict the As concentration of the river water. Moreover, the plants (average 412 mg As/kg^{-1}) contained around 10 times the As concentration of the sediments (average 46 mg As/kg^{-1}) that, in turn, had over 1000 times the As concentration of the ambient water (average 0.042 mg As/L^{-1}). In this case, *Ceratophyllum demersum* provides an excellent bioindicator for As.

Other factors, such as the pH, water temperature and nutrient availability, doubtless affect As accumulation. Further work needs to be carried out on these effects to determine how well these bioindicators would perform under various scenarios. This study and earlier studies analyzed whole specimens of *C. demersum* rather than stems and leaves. Leaves and stems could well have different As concentrations and hence different bioaccumulation coefficients.

Aquatic macrophytes for the phytoremediation of As-contaminated water

The high bioaccumulation factor of aquatic plants may make them useful for the phytoremediation of As from contaminated drinking water. The possibility of using plants to remove As has been discussed by Brooks and Robinson (1998). More generally, the use of aquatic plants to remove pollutants from water has been outlined by Wolverton (1975), Wolverton and McDonald (1975a, 1975b) and Nzengung et al. (2003).

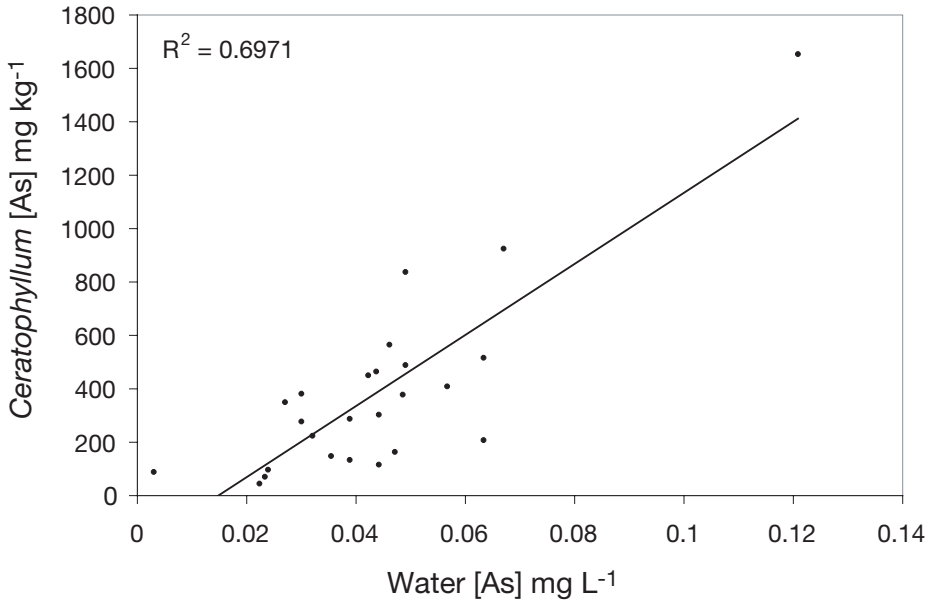

Figure 12.3 Relationship between plant As concentration in Ceratophyllum demersum (mg/kg^{-1} dry matter) and that of the ambient water (mg/L-1) along the Waikato River

Reworked data from Robinson et al. (1995a)

Two methods have been suggested for using plants for the phytoremediation of contaminated water (Brooks 1998). The first involves the use of free-floating plants growing in monospecific pond cultures. Plants accumulate As until an equilibrium state is reached, then harvested. There are several problems related to this method. The main problem is harvesting of the plant matter enriched with the contaminant; a secondary problem relative to monospecific cultures is the risk of developing a plant disease that can destroy the whole crop. The second method is set up using rooted plants growing in trickling-bed filters. In this case, it is hypothesized that metal uptake is caused by rhizosphere microorganisms with just a small contribution of plant roots (Brooks 1998).

Aquatic plants could therefore provide a very efficient means for removing As from contaminated drinking-water. Plants would be grown in ponds containing contaminated water, then simply removed and placed in an area where they do not pose a risk to the environment, such as a sealed landfill. Very simple low-cost technology such as this could potentially save lives in developing countries that cannot afford expensive water purification systems.

Arsenic contamination of food chain

Arsenic accumulation by aquatic macrophytes may facilitate the entry of this toxic element into the food chain (Chapters xx–xx). Plants are the primary producers of most food chains. Humans may be directly affected if plants such as watercress and mint are consumed, or indirectly when they consume species that have high As levels due to contamination of the food chain. Much of the Waikato River is surrounded by farmland and stock may occasionally have access to aquatic weeds left on the banks after a flood. Fishing is also popular in the region. However, an earlier study (Robinson et al. 1995b) showed that total As levels in fish were below the WHO limit for As in foodstuffs (i.e. 2.0 mg/kg^{-1}).

In a lake or river system, the amount of plant-bound As at any one time may be a significant portion of the total amount of As in the river. Therefore if, for example, drought or pesticides

kill the plants, there may be a large pulse of As released into the water as the plants decay. The depuration of As by these plants has not been tested.

Watercress should not be taken from zones where there may be elevated As concentrations in aquatic systems. This is particularly relevant in geothermal areas where As-rich geothermal fluids increase the As burden on aquatic systems. The development of geothermal power stations and geothermal heating systems that discharge geothermal fluids into waterways may render previously safe locations unsuitable for watercress collection.

Conclusions

There is a clear distinction between aquatic and terrestrial plants regarding their ability to accumulate As. Obviously, the reported terrestrial As hyperaccumulators have specialized mechanisms that allow them to solubilize, take-up and store As in a non-toxic form. Arsenic accumulation is widespread among aquatic plants, and this study identified new As hyperaccumulator species. More species will undoubtedly be found as further surveying is conducted.

Arsenic accumulation by aquatic macrophytes may make them valuable tools for the bioindication and phytoremediation of As. Additionally, the ecological impacts of As accumulation are likely to be profound.

One unresolved question is whether As is incorporated into the cells of aquatic macrophytes, or simply deposited/precipitated onto the surface of the plant. In the latter case, it could be argued that the plants are not true hyperaccumulators as they may lack specialized As uptake and storage mechanisms. Nevertheless, this does not change their potential usefulness as bioindicators or for phytoremediation, or make them any less toxic if consumed.

Further work is warranted to elucidate the mechanisms of As accumulation in aquatic species. The question of how aquatic macrophytes accumulate As could be partially resolved by conducting microanalyses on the tissues to determine whether As is present inside the cells or simply bound to the cell walls.

References

Aggett J & Aspell AC (1978). *Arsenic from geothermal sources*. New Zealand Research and Development Committee Report No. 35.

Axtmann RC (1975). Environmental impact of a geothermal power plant. *Sci.* 187: 795–803.

Brandsetter A, Lombi E, Wenzel WW & Adriano DC (2001). Arsenic contaminated soils: I. Risk assessment. In *Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals* (ed DC Adriano), 2nd edn, Springer, New York: 715–737.

Brooks RR & Robinson BH (1998). Aquatic phytoremediation by accumulator plants. In *Plants that hyperaccumulate heavy metals: their role in archaeology, microbiology, mineral exploration, phytomining and phytoremediation* (ed RR Brooks), CAB International, Wallingford: 203–226.

Brooks RR, Lee J, Reeves RD & Jaffré T (1977). Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *J. GeoChem. Explor.* 7: 49–77.

Forstner U & Wittmann GTW (1981). *Metal pollution in the aquatic environment* (Springer-Verlag, New York.

Freeman MC (1985). The reduction of arsenate to arsenite by an *Anabaena* bacteria assemblage isolated from the Waikato River. *NZ J. Marine & Freshwater Res.* 19: 277–282.

Hill CF (1975). Impounded lakes of the Waikato River. In *New Zealand lakes* (ed VH Jolly & JMA Brown), Auckland University Press, Auckland.

Khattak AK, Page AL, Parker DR & Bakhtar D (1991). Accumulation and interactions of arsenic, selenium, molybdenum and phosphorus in Alfalfa. *J. Environ. Qual.* 20: 165–168.

Liddle JR (1982). Arsenic and other elements of geothermal origin in the Taupo Volcanic Zone. PhD thesis, Massey University, Palmerston North, New Zealand.

Ma LQ, Komar KM, Tu C, Zhang W, Cai Y & Kennelly ED (2001). A fern that hyperaccumulates arsenic. *Nature* 409: 579.

Manning BA & Goldberg S (1997). Arsenic (III) and arsenic (V) adsorption on three California soils. *Soil Sci.* 162: 886–895.

Meharg AA & Macnair MR (1991). Uptake, accumulation and translocation of arsenate in arsenate-tolerant and non-tolerant *Holcus lanatus* L. *New Phytol.* 117: 225–231.

Metcalf L (1993). *The cultivation of New Zealand plants*, Godwit Press, Singapore.

Nzengung VA, O'Neill WL, McCutcheon SC & Wolfe NL (2003). Sequestration and transformation of water soluble halogenated organic compounds using aquatic plants, algae, and microbial mats. In *Phytoremediation transformation and control of contaminants* (eds SC McCutcheon & JL Schnoor), John Wiley & Sons, New Jersey, : 499–528.

Outridge PM & Noller BN (1991). Accumulation of toxic trace elements by freshwater vascular plants. *Rev. Environ. Contam. Toxicol.* 121:163.

Pepper I, Galanti N, Sans J & Lopez-Saez JF (1987). Reversible inhibition of root growth and cell proliferation by pentavalent arsenic in *Allium cepa*. *Environ. Exp. Bot.* 28(1): 9–18.

Pickering IJ, Prince RC, George MJ, Smith RD, George GN & Salt DE (2000). Reduction and coordination of arsenic in Indian mustard. *Plant Physiol.* 122: 1171–1177.

Raven KP, Jain A & Loeppert RH (1998). Arsenite and arsenate adsorption of ferrihydrite: kinetiks, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* 32: 344–349.

Reay PF (1972). The accumulation of arsenic from arsenic-rich natural waters by aquatic plants. *J. Appl. Ecol.* 9: 557–565.

Robinson BH, Brooks RR, Outred HA & Kirkman JH (1995a). The distribution and fate of arsenic in the Waikato River system, North Island, New Zealand. *Chem. Speciation Bioavail.* 7(3): 89–96.

Robinson BH, Brooks RR, Outred HA & Kirkman JH (1995b). Mercury and arsenic in trout from the Taupo Volcanic Zone and Waikato River, North Island, New Zealand. *Chem. Speciation Bioavail.* 7(1): 27–32.

Robinson BH, Mills TM, Petit D, Fung LE, Green SR & Clothier BE (2000). Natural and induced cadmium-accumulation in poplar and willow: implications for phytoremediation. *Plant and Soil* 227: 301–306.

Robinson BH, Duwig C, Bolan NS, Kannathasan M & Saravanan A (2003). Uptake of arsenic by New Zealand watercress (*Lepidium sativum*). *Sci. Total Environ.* 301(1): 67–73.

Smies J (1983). Biological aspects of trace element speciation in the aquatic environment. In *Trace element speciation in surface waters and its ecological implications* (ed GG Leppard), Plenum Press, New York: 177–193.

Smith E, Naidu R & Alston AM (1999). Chemistry of arsenic in soils: I. Sorption of arsenate and arsenite by four Australian soils. *J. Environ. Qual.* 28: 1719–1726.

Tanner CC & Clayton JS (1990). Persistence of arsenic 24 years after sodium arsenite herbicide application to Lake Rotoroa, Hamilton, New Zealand. *NZ J. Marine Fresh Water Res.* 24: 173–179.

Tyler G & Olsson T (2001). Concentration of 60 elements in the soil solutions as related to the soil acidity. *Eur. J. Soil Sci.* 52: 151–165.

Wolverton BC (1975). *Water hyacinths for removal of cadmium and nickel from polluted waters.* NASA Technical Memorandum TM-X–72721.

Wolverton BC & McDonald RC (1975a). *Water hyacinths and alligator weeds for removal of lead and mercury from polluted waters*. NASA Technical Memorandum TM-X–72723.

Wolverton BC & McDonald RC (1975b). *Water hyacinths and alligator weeds for removal of silver, cobalt and strontium from polluted waters*. NASA Technical Memorandum TM-X–72727.