VARIABILITY, SPECIATION AND PHYTOREMEDIATION OF SOIL ARSENIC AT CATTLE DIP SITES IN NSW, AUSTRALIA

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CERTIICATE OF ORIGINALITY

I hereby declare that the text of this thesis is my own work, and that, to the best of my knowledge and belief, it contains no material that has been previously published or written by another person, nor any material that has been accepted as part of the requirements for any other degree or diploma in any university or other institute of higher learning, unless due acknowledgement has been made.

I also declare that the intellectual content of this thesis is original and the result of my own research and to the best of my knowledge and belief, any assistance I received in the experimentation presented, and all sources of information cited have been duly acknowledged.

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Nabeel Khan Niazi

Declared at The University of Sydney

this 31st day of

August 2011

TO
MY PARENTS
AND FAMILY

ABSTRACT

Arsenic (As) contamination of soils is a major environmental problem due to its toxic and carcinogenic nature. Historical use of As-containing pesticides has resulted in the contamination of soils with high and variable concentrations of As in many parts of Australia. Phytoremediation using As-hyperaccumulating ferns can be potentially utilised as an environmental friendly and low-cost remediation technology to phytoextract As from soils at sites containing elevated and varying concentration of As.

The spatial variability of total and phosphate-extractable As concentrations was evaluated in soil adjacent to a cattle-dip site located at Wollongbar in northern NSW, Australia. The results from the linear mixed model showed that total (0–0.2 m) and phosphate-extractable (0–0.2, 0.2–0.4 and 0.4–0.6 m depths) As concentrations in the soil adjacent to the dip site varied greatly and increased significantly (P = 0.004–0.048) toward the dip site, indicating that As variability in soil was spatially correlated with distance from the dip. The data suggest that 5 samples should be required to assess the soil contamination level (mean = 826 mg kg^{-1}) and 15 samples would be required to evaluate the effects of phytoremediation of As-contaminated site. The proposed guidelines on sampling requirements are important to estimate the variability in As contamination levels around other cattle-dip sites and to monitor changes in soil As content from phytoremediation activities.

Ensuing study compared the phytoremediation potential of *Pityrogramma calomelanos* var. *austroamericana* (gold dust fern) against the well-known *Pteris vittata* (Chinese brake fern) over a 27-month duration grown at the cattle-dip site described earlier. The ferns were planted in January 2009 and harvested following 10, 22 and 27 months of growth. After 10 months of

growth (short-term data), *P. calomelanos* var. *austroamericana* produced significantly higher frond dry biomass, possessed higher frond As concentration and removed more As in fronds (mean = 130 g plant^{-1}, 887 mg kg^{-1} and 124 mg plant^{-1}, respectively; $P < 0.05$) than *P. vittata* (mean = 81 g plant^{-1}, 674 mg kg^{-1}, 57 mg plant^{-1}). Further samplings up to 27 months (long-term data) confirmed the earlier results that the mean frond dry biomass, As concentration and As uptake were significantly higher in *P. calomelanos* var. *austroamericana* than *P. vittata*. In the three harvests over the 27-month period, *P. calomelanos* var. *austroamericana* removed (8,053 mg As) 2.65 times higher As than *P. vittata* (3,042 mg As). For the surface (0–20 cm) and subsurface (40–60 cm) layers, the mean total soil As content was significantly ($P < 0.05$) reduced by 49% and 63%, respectively, using *P. calomelanos* var. *austroamericana*; and 17% and 15%, respectively, by *P. vittata* ($P > 0.05$). It is estimated that *P. calomelanos* var. *austroamericana* would take approximately 6 years to decrease mean total As content below the ecological investigation level (EIL; 20 mg kg^{-1}) limit in the surface and subsurface soils, whereas *P. vittata* would require 13–15 years to achieve this target. The field experiment results suggest that *P. calomelanos* var. *austroamericana* is better suited than *P. vittata* for the phytoremediation of As-contaminated soils under the experimental conditions existing at the site.

The potential of mid infrared (MIR) spectroscopy in combination with partial least squares (PLS) regression was investigated to estimate the total As content in a large number of soil samples collected from a highly variable As-contaminated dip site. The MIR-PLS calibration model developed excluding spectral outliers (n = 149) was robust with an acceptable reliability (coefficient of determination; R^2_c = 0.73; residual prediction deviation; RPD_c = 1.94) to estimate total soil As content. The validation of calibration model using a separate set of unknown soil samples (n = 149; validation set) showed R^2_v and RPD_v values of 0.63 and

1.66, respectively. The results indicate an acceptable prediction of total As content in unknown samples, suggesting that MIR-PLS based model is capable of estimating total soil As and possibly be used in certain situations; for example to estimate soil As concentration at a highly variable site, where a large number of samples needs to be analysed.

The solid-phase speciation and plant availability of As in contaminated soils was determined using combination of a sequential extraction procedure (SEP), X-ray absorption near edge structure (XANES) spectroscopy and As plant uptake using *Brassica juncea* as a test plant. Arsenic was found to be predominantly associated with amorphous Fe oxides in arsenate (As^{V}) form; in few samples As was present in arsenite (As^{III}) form. The concentration of As in plant shoots showed significant ($P < 0.001–0.05$) correlations with the exchangeable As ($r = 0.85$), and amorphous Fe oxides associated As evaluated by the SEP ($r = 0.67$) and XANES spectroscopy ($r = 0.51$). The results suggest that As in these fractions is readily available for plant uptake and may pose potential risk to the environment. Such detailed analysis for As speciation and phytoavailability is vital for the management and rehabilitation of As-contaminated soils.

* * *

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2. Niazi NK, Singh B, Shah P (2011) Arsenic speciation and phytoavailability in contaminated soils using a sequential extraction procedure and XANES spectroscopy. *Environmental Science & Technology* 45 (17):7135–7142.

3. Niazi NK, Bishop TFA, Singh B, (2011) Evaluation of spatial variability of soil arsenic adjacent to a disused cattle-dip site, using model-based geostatistics. *Environmental Science & Technology* 45 (24):10463–10470.

4. Niazi NK, Singh B, Van Zwieten L, Kachenko AG (2011) Phytoremediation of an arsenic contaminated site using *Pteris vittata* L. and *Pityrogramma calomelanos* var. *austroamericana*: a long-term study. *Environmental Science and Pollution Research* (Submitted).

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5. Niazi NK and Singh B (2011) Using mid infrared (MIR) spectroscopy and partial least-squares regression to predict total soil arsenic content at a highly variable site. *Environmental Science & Technology* (In preparation).

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6. Niazi NK, Singh B, Zwieten LV and Kachenko, AG (2010) Arsenic hyperaccummulation by ferns: a field study in northern NSW. *Published paper in the Proceedings of the 19th World Congress of Soil Science on Soil Solutions for the Changing World*. Brisbane, Australia, 1–6 August 2010, pp. 5–8.

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7. Niazi NK and Kachenko AG (2011) Letter to the Editor regarding, "First evidence on different transportation modes of arsenic and phosphorus in arsenic hyperaccumulator *Pteris vittata*" by Lei et al. (2012). *Environmental Pollution* (Article in press) doi: 10.1016/j.envpol.2011.11.031.

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8. Niazi NK, Singh B, Shah, P (2010) Speciation and bioavailability of arsenic in contaminated soils using X-ray absorption near edge structure spectroscopy and a sequential extraction procedure. *Proceedings of ConSoil International Conference on the Management of Groundwater, Soil & Sediments*. Salzburg, Austria, 21–24 September, 2010 (Oral presentation).

9. Niazi NK, Bishop T, Singh B, (2010) Comparative study for the arsenic hyperaccumulation by ferns: a model-based geostatistical approach. *Proceedings of ConSoil International Conference on the Management of Groundwater, Soil & Sediments*. Salzburg, Austria, 21–24 September, 2010 (Poster presentation).

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