# 19th World Congress of Soil Science

# Symposium 3.5.2

# Risk assessment and risk based remediation

**Soil Solutions for a Changing World,**

**Brisbane, Australia**

**1 – 6 August 2010**

# Table of Contents

## Table of Contents (cont.)

**Page**

# Accumulation, transfer and environmental risk of soil mercury in a rapidly industrializing region of the Yangtze River Delta, China

**Biao Huang[A]**, Mei Wang[A], Weixia Sun[A] and Yongcun Zhao[A]

[A]Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China, Email bhuang@issas.ac.cn, mwang@issas.ac.cn, wxsun@issas.ac.cn, yczhao@issas.ac.cn

## Abstract

Mercury (Hg) accumulation and transfer in soil-plant ecosystems have increased concern. A region at county level under rapid industrialization and intensive agricultural activities in the Yangtze River Delta of China and a factory with Hg-containing wastewater discharge within the region were selected to study the accumulation and transfer of Hg from different sources in soils and crops. The results showed significant Hg accumulations in soils away from factories and enhancement of mobile HCl-extractable Hg concentrations in the soils close to factories due related to soil pH and organic matter. Soil and crop Hg accumulations around the factory were localized and exponentially decreased with distance away from the discharge outlet. Considering the cessation of Hg-containing agrochemicals and limitation of effects of industrial activities on Hg accumulation, more attention should be paid to changing in soil properties and crop rotations because the current risk is mobilization of accumulated soil Hg.

## Key Words

Soil mercury bioavailability, spatial variability, agricultural and industrial sources, soil-crop ecosystem.

## Introduction

With economic and industrial development, increased loading of mercury (Hg) in the environment and the potential public health risk associated with dietary intake have increasingly become a concern. Although the Chinese government has forbidden the use of Hg-containing fertilizer and pesticides since the 1970s, industrial discharges might aggravate the environmental potential threat of soil Hg accumulation and complicate the tracing of environmental Hg sources due to rapid industrialization in recent decades.

Most underlying studies related to Hg accumulation and soil-crop transfer were concentrated on the areas where Hg mainly originated from the atmosphere. However, waste effluent from certain types of factories may also cause Hg accumulation and transfer. With rapid urbanization and industrialization in the Yangtze River Delta, a lot of factories were built up and scattered in agricultural lands. Meanwhile, intensive farming was conducted due to the demands for agricultural products from this urban area. The degree and the extent of Hg accumulation in soil and crops under such complicated situations remain unclear. The specific objectives of this study are: (1) to investigate the distribution of soil Hg in the Zhangjiagang County area, Yangtze River Delta of China; (2) to evaluate and characterize the spatial distribution and transfer of Hg in soil-crops around the factory, a point source of Hg; and (3) to reveal and assess the potential Hg contamination threat to the environment.

## Materials and methods

### Study area

The study area, Zhangjiagang County, is situated on a flat alluvial plain in the Yangtze River Delta. The main soil types can be divided into two soil orders, Anthrosols (Inceptisols) and Cambosols (Entisols). The rotation of rice and wheat has been the dominant planting system, though historically cotton-wheat was more common on Cambosols. Historically, Hg-containing pesticides had been used for cotton and rice planting in this area. Since the 1980s, Zhangjiagang County has become one of the quickest economically developing areas in the Yangtze River Delta region, and industry mainly flourishes including metallurgical, chemical, electroplating, printing and dyeing, paper-making, etc.

### Sample collection and preparation

Within the county, a total of 547 samples of the topsoil (0-20 cm) were collected, of which 386 samples were randomly collected on agricultural land away from the factories throughout the county based on soil types, land use, spatial homogeneity. 161 samples were also collected on agricultural land at ca. 50-100 m from waste discharging factories. An intensive sampling, including soil and crop sampling, was conducted around

the factory with the highest soil T-Hg in order to evaluate the effect of increased Hg in soil on spatial distribution of Hg in soil and crop Hg uptake. Soil basic properties such as soil pH and organic matter (OM), 1 M HCl-extractable Hg (HCl-Hg) and Total Hg (T-Hg) in soils, and Hg in rice and wheat were examined. The Hg fractionation of soils from profile horizons was analyzed for evaluating detailed information on the mobility of Hg in samples.

**Results**

*Distribution of regional soil Hg and soil properties*
Soil T-Hg in the Cambosols was greater than that of Anthrosols (p < 0.05) (Table 1), which also shows the frequency and spatial distribution patterns of soil T-Hg. Interestingly, two frequency peaks of soil T-Hg are evident with each respective soil order, in particular, Cambosols. Sampling locations also influenced the soil T-Hg concentrations significantly. The average soil T-Hg concentration for sampling sites far away from the factories was significantly higher ($p<0.05$) than that of sites close to the factories(Table 1). But, the highest levels of soil T-Hg appeared in the sites close to the factory, where we sampled intensively.

With soil T-Hg, soil order had a significant effect on HCl-Hg, resulting in a lower soil HCl-Hg in Cambosols than that in Anthrosols. However, without soil T-Hg, the HCl-Hg for sampling sites close to factories was significantly greater than that of the sites away from factories ($p<0.05$).

**Table 1.  Hg contents in surface soils classified by soil orders and sampling site.**

|  | No. | Available Hg (µg/kg) | No. | Total Hg (µg/kg) | SOM (g/kg) | pH |
|---|---|---|---|---|---|---|
| Cambosols | 37 | 35.7a | 353 | 125a | 19.40a | 7.63b |
| Anthrosols | 16 | 46.6b | 194 | 167b | 25.17b | 7.00a |
| Away from factories | 31 | 32.4a | 359 | 149b | 20.98a | 7.67b |
| Close to factories | 22 | 48.1b | 188 | 121a | 22.32b | 6.91a |

*Distribution of soil and crop Hg close to factory*
In the spatial context, the highest T-Hg and HCl-Hg concentrations were found near the wastewater outlet (about 50 m away from the outlet) and then the T-Hg and HCl-Hg exponentially decreased as distance from the outlet increased.
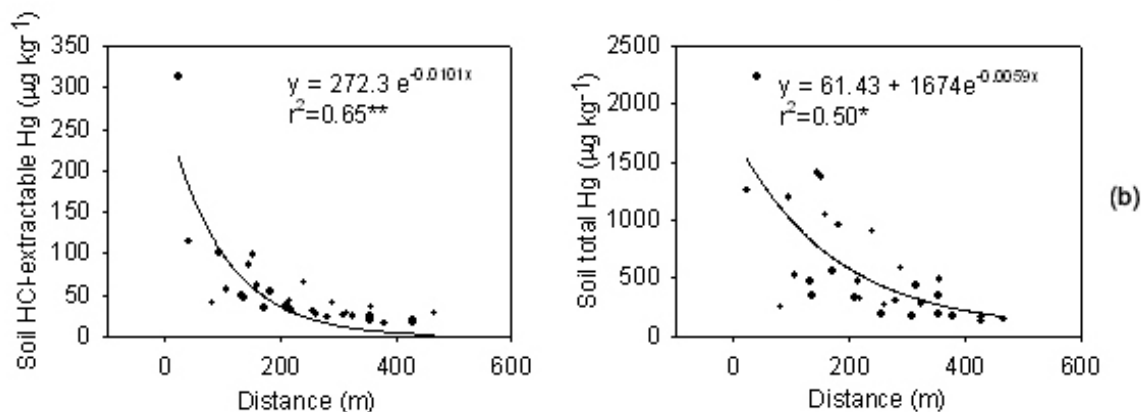


**Figure 1. Soil Hg distribution in surface soil around the factory (a) and the soil Hg variability with the distance from the wastewater outlet**

In the soil profile near the outlet, the uppermost soil horizon (0-15 cm) had high T-Hg and HCl-Hg concentrations. Total Hg concentrations reached a peak at the 10-15 cm depth (2711 µg/kg), and then rapidly decreased with depth. Lowest T-Hg concentration (94 µg/kg) was below 50 cm in the profile. Likewise, the HCl-Hg concentrations reached a peak at 10-15 cm deep (115 µg/kg) and then decreased with increasing depth. Lowest HCl-Hg concentration (24 µg/kg) was below 50 cm in the profile. The surface soil of the profile nearby the outlet had higher the percentages of mobile and semi-mobile Hg fractions relative T-Hg than those of to profiles away from the outlet.  Hg concentrations in rice grain were nearly 5 times higher than those in wheat grain. There were variable trends in distribution between wheat and rice Hg for plants in close proximity to the wastewater outlet. For rice, the high Hg concentrations (above 15 µg/kg) were found within 200 m from the wastewater outlet, and Hg concentrations in rice exponentially decreased with the distance from the outlet. No such a trend was found for uptake of Hg by wheat.

## Discussion and conclusions
*Regional risk assessment of soil Hg*
Compared to the critical value of Chinese Environmental Quality Standards for Soil (CEQS), no soil T-Hg concentrations exceeded the second most stringent critical value (500 µg/kg when pH>6.5) in the Cambosols area, while soil Hg at 6 sampling sites in the acidic Anthrosols area exceeded the critical value of CEQS (300 µg/kg when pH<6.5), among which 5 of 6 sites was located in the sites away from factories and the other one was the site close to the chemical factory, where we did intensive sampling. Because of the historically wide uses of Hg-containing pesticides for cotton and rice planting in the county, it could be inferred that the accumulation of soil Hg probably originated mainly from agricultural activities. As for industrial sources of soil Hg accumulation, the influences might be only localized, which is verified by a lower soil T-Hg at the sites close to factories than the sites away from factories (Table 1) despite a very high level of soil T-Hg that was found close to the factory's wastewater outlet.

Although the Hg-containing pesticides have been prohibited for production and use since the 1970s in China and the risk of Hg accumulation in the county is very limited, it should be noted that the changes of soil properties such as soil pH and OM in the studied area may increase the environmental risk. A stepwise regression of soil HCl-Hg against soil T-Hg, pH, and OM has confirmed that the $r^2$ (0.38) of the stepwise regression had a significant increase compared to the $r^2$ (0.27) of the regression between soil HCl-Hg and T-Hg, which indicates that available HCl-Hg could increase with decreasing soil pH and increasing soil OM, even though the soil T-Hg is not changed. Hence, when the soil use conversion is conducted, soil pH and HCl-Hg should be monitored.

*Risk assessment of soil Hg accumulation by industrial activities*
Exponential decreases of soil Hg with distance from the outlet indicated that the accumulation range was limited spatially. However, the accumulated levels of soil T-Hg and HCl-Hg was so high that some of the rice Hg concentrations were over the critical value of Hg in crops (20 µg Hg/kg) according to the maximum allowable levels of contaminants in foods (MALCF) of China (GB2762-2005). Therefore, effective measurements should be conducted to reduce Hg in the wastewater and control discharges to the surface water.

*Risk assessment of crop Hg*
The wheat samples did not exceed the MALCF level. However, 2 out of 15 rice samples exceeded the MALCF, indicating some Hg pollution in rice. Concentrations of Hg in rice grain were 5 times as high as wheat grain, suggesting a stronger Hg uptake by rice than wheat, which may be attributed to reduction of soil under water logged conditions during rice growing, which increased the availability of Hg, and, consequently, the uptake by rice or direct Hg uptake from wastewater.

# Bioremediation of crude oil polluted soil as affected by sewage-sludge

**Mostafa Chorom**[A], Sara Sharifi Hosseini[B] and Hossein Motamedi [C]

[A]Soil Science dept.,College of Agri.,Shaid Chamran University, Khuzstan, Iran Email mchorom@yahoo.com
[B]Soil fertility and sustainable development research, jehade daneshghie khuzstan, Iran.
[C]Biology dept., College of Science, Shaid Chamran University, Khuzstan, Iran.

## Abstract

During the Persian Gulf war in 1991 around eight million barrels of crude oil were spilled into water. This caused a large volume of contaminated water has to move to land in particular, Khuzestan's soil. A real danger of oil pollution would be an environmental calamity, and therefore, reclamation practice on the spoil soil area to expel the oil is essential. Bioremediation methods will be surveyed. In this study the soil artificially polluted with 1% density of crude oil and sewage sludge were applied at 3 levels of 0, 50 and 100 ton/h equivalent to the field application. These soils were kept at 30°C and 60 percent of F.C. for 5 to 10 weeks. The soils were then analyzed for hydrocarbon-degrading, heterophic bacteria count and some other soil chemical properties. Oil degradation was measured by a Soxhlet extraction method, and gas chromatography. Data indicated that treatments caused the degradation of 45% to 60% of oil in contaminated soil. The results showed that the degrading heterotrophic bacteria population increased from $6\times10^3$ cfc/gr in control soil to $2\times10^{10}$ cfc/gr in treated soil and C/N ratio decreased from 6 to less than 3. Gas chromatography results also showed a decrease in normal paraffin and isopernoids, like phytane and pristine.

## Key Words

Bioremediation, heterotrophic bacteria, gas chromatography, isopernoids.

## Introduction

In recent year there has been a high demand for crude oil as a primary source of energy in civilized societies. Its market value and consumption of its end products have caused a huge increase in production of crude oil. This further encouraged more refineries and photo chemical industries and the need to exploit and drill for more oil to some extent ignoring the consequence of such activities on the environment and human life. Bioremediation is a useful method for improving oil contaminated soils. In this method living microscopic creatures use the hydro carbonic materials as food and energy resource and then change them easily to non poisonous materials like water and carbon-dioxide.

The result of this process is to reduce the oil hydrocarbons in soil (Espinoza and Dendooven 2003). Bioremediation is intermediate between engineering and natural methods and involves human interference like agricultural practices (plowing, fertilizing and etc) in order to promote suitable living conditions for microscopic soil creatures and increases the degradation of soil pollutants. Also, use of palliative materials like applying organic matter with nitrogen and phosphorus and plowing in order to ventilate the soil in a better way are beneficial. This may help to increase the microbial activity by bacteria and fungi. Namkoong *et al.* (2002) in bioremediation of diesel oil contaminated soil found that mixing the polluted soil with sewage-sludge on a volume of 0.5:1 showed the highest palliative degradation. Gogoi *et al.* (2003) in bioremediation of crude oil polluted soil have observed that ventilation, using organic matters with nitrogen and phosphorus and microbes insemination has lead to the demolition of 75 percent of the contamination factors. Therefore, the aim of this research was to evaluate the effects of sewage sludge application as organic fertilizer on stimulating biological processes and crude-oil bioremediation oil polluted soil.

## Methods

Uncontaminated soil was taken from field, air dried and passed through a 2mm sieve. Then, this soil was contaminated by crude oil at rate of 1% weight artificially. The crude oil which was delivered from well No. 69 of the Maroon oil field is paraffin oil (Figure 1). The soil samples were kept for two weeks then divided into 5 kg portions and stored in special containers. Dry  sewage sludge was prepared from the south sewage refinery of Ahvaz and after crushing and passing through a 2 mm sieve was added to the soil at the rates of 0, 50, 100 ton/ha. The soil treatments were kept under controlled humidity 60 percent of F.C. and 30°C. In order to having aerobic soils conditions, they were stirred thoroughly twice a week for 5 to 10 weeks. At the end of this period the soil samples were removed, air dried and passed through a 2 mm sieve. The soils were analyzed for hydrocarbon-degrading, heterophic bacteria and some soil chemical properties. Oil remaining

was measured by a Soxhlet extraction method, and gas chromatography. Hydrocarbon-degrading heterotrophic bacteria were determined using a MPN method.
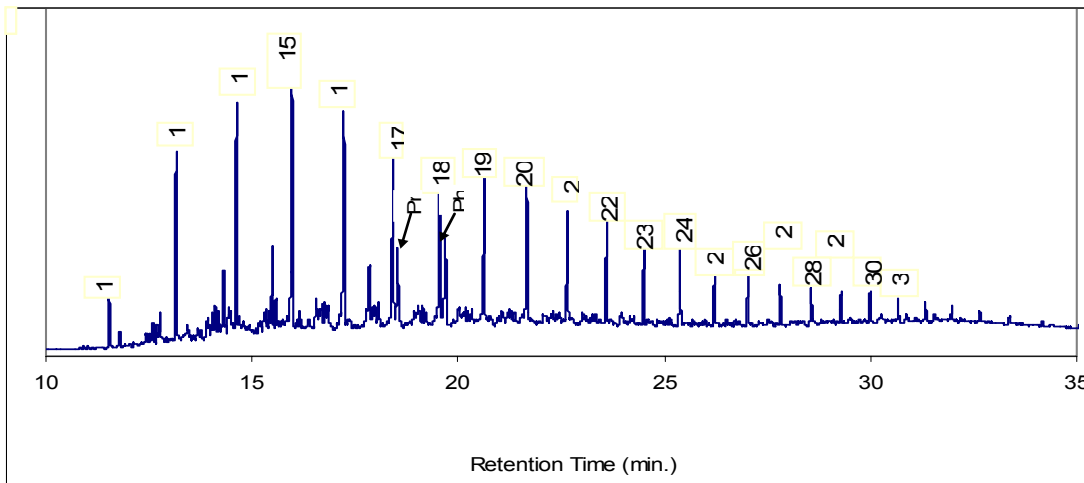


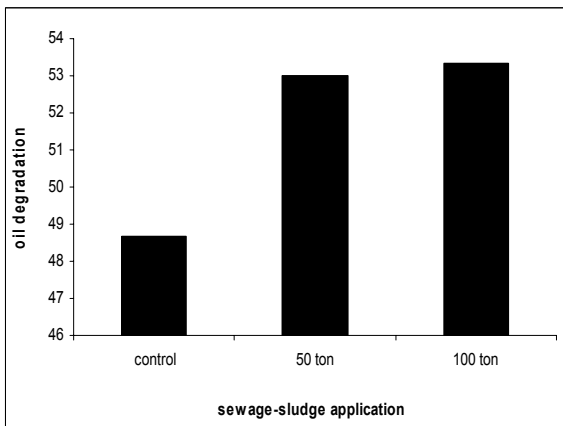**Figure 1. GC of crude oil sample from 69 well**



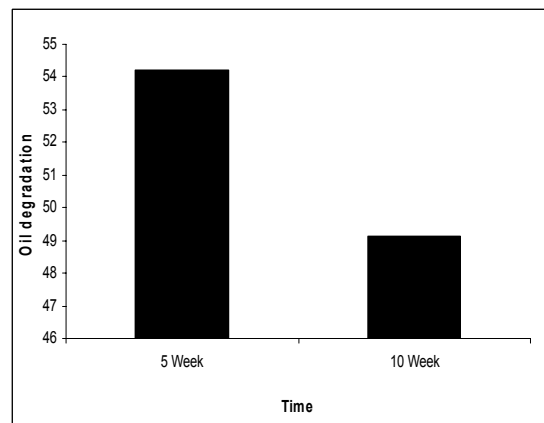**Figure 2. The effect of sewage-sludge treatments on oil degradation.**



**Figure 3. The effect of time on oil degradation.**
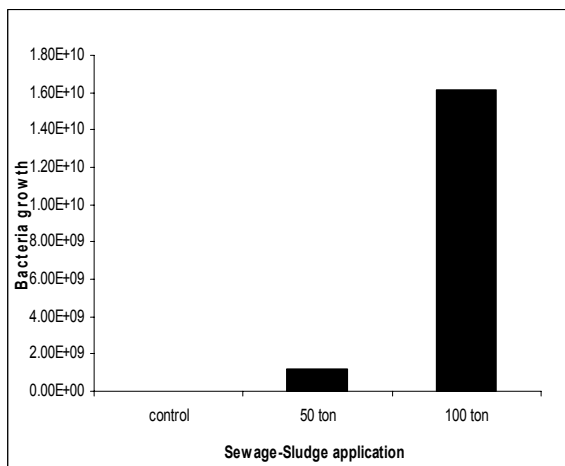


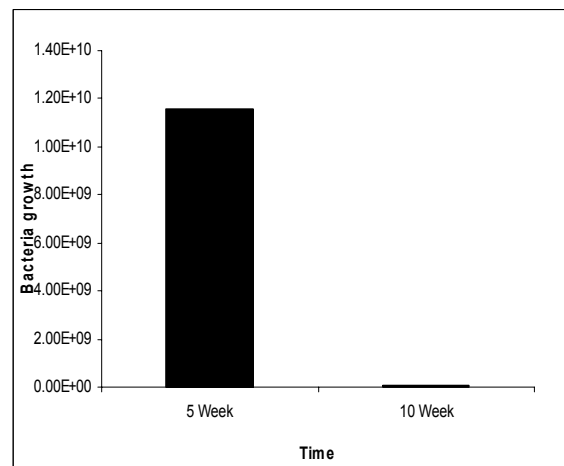**Figure 4. The effect of sewage-sludge treatments on bacteria growth.**
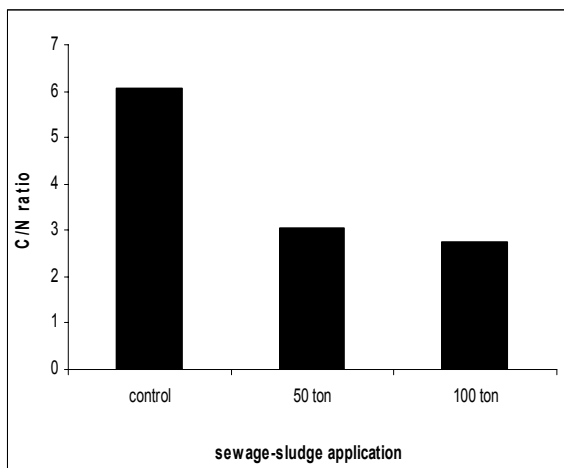


**Figure 5. The effect of time on Bacteria growth.**

**Figure 6. The effect of sewage-sludge treatments on C/N ratio.**
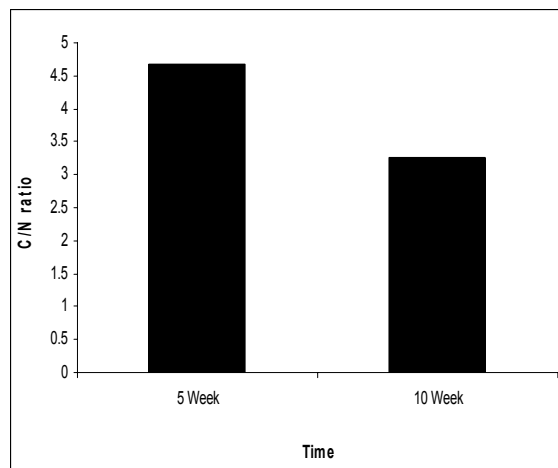


**Figure7. The effect of time on C/N ratio.**

## Results

The results showed that addition of sewage sludge and soil ventilation caused an increase heterotrophic growth and petroleum degradation (Figures 2 and 3). The effect of the 100 ton/ha sewage-sludge application on petroleum degradation was more than 50 ton/ha. Under controlled environment when soil has more ventilation normal condition suitable for bacteria activity were observed (Figures 2 and 3). Espinosa and Dendooven (2003) showed that the added organic matter like sewage sludge to the polluted soil would quicken bioremediation of diesel oil and TPH because of interring a great deal of nutrition materials. The effect of time on petroleum degradation was significant and this observation corresponded with the bacteria growth results (Figures 4 and 5). The highest bacteria growth was achieved after 5 weeks, the presence of paraffin and organic nutrition materials, result in decomposing petroleum and enhanced bacteria activity to a maximum rate. The results showed a significant difference between the various treatment effects of sewage-sludge on soil C/N ratio. As is observed in Figure 6, C/N ratio of 6 in control samples changed to 3. C/N ratio initially decreased but by the fifth week the proportion was higher than the 10th week (Figure 7), because in the fifth week there was suitable feeding materials available for bacteria, and with passing of time the level of organic matters appear to lower little by little and would limit bacteria growth and oil degradation. Though this procedure of organic matter sewage sludge would release and become feeding materials in the dissolved material that it is creating a suitable nutrition condition which cause the increment of oil degrader heterotrophic bacteria. Ramsy *et al.* (2000) observed that continual ventilation and fertilizer increment will have a considerable effect on the growth of hydro carbonic degrader bacteria in soil. In the present research during 5 weeks the presence of normal paraffin and environmental conditions with appropriate feeding, bacteria growth and oil degradation were high, but in 10 weeks aromatic and remaining asphalted component with no nutrition elements caused to decrease the bioremediation process (4). Lee *et al.* (2007) showed that fertilizing effect on biological stimulate of local bacteria soil and process, decreases with time. In order to facilitate the normal paraffin change survey, on the base of their chemical nearness combination they are divided in to 6 classes as follows: <C13, C13-C16, C17-C21, C22-C25, C26-C29, C30-C36. Paraffin's class C13-C16, C26-C29, C30 were much degraded by heterotrophic bacteria in comparison to control sample (Figures 8 and 9). Changes in the medium chain paraffin like treatment required 50 tones of sewage sludge showed about 50% decrease in comparison to control which expresses the low tendency of hydro carbonic degrader heterotrophic bacteria for the degradation of singular normal paraffin's in these paraffin's which resulted of their primary source. With passing of 10 weeks of sewage sludge application as organic fertilizer for microbial degradation, class C30-C36 had increased significantly from 2% to 62% that showed the microbes tendency for decomposing high chain normal paraffin's (Figure 9). Classes C17-C21, C22-C25, and C26-C29 hydrocarbon degraded 37%, 22% and 69% respectively.
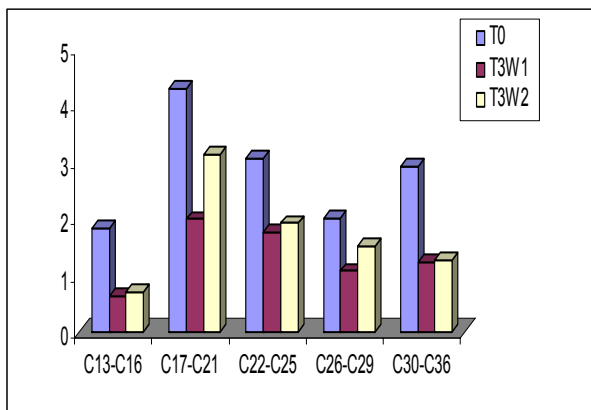
**Figure 8. Comparison of percentage normal alkenes classes after 50 ton/ha  Sewage-sludge application of 5/10 weeks as T3W1/T3W2.**
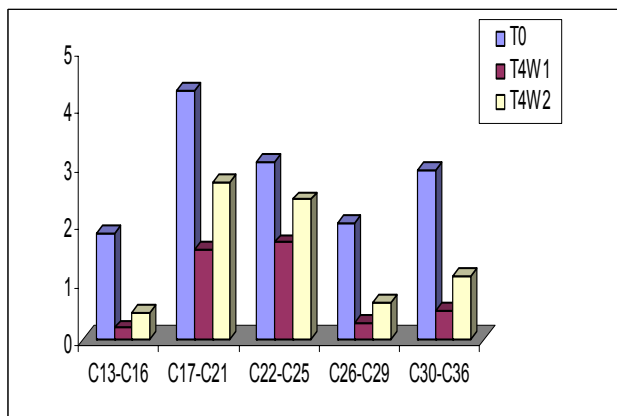
**Figure 9. Comparison of percentage normal alkenes classes after 100 ton/ha  Sewage-sludge application of 5/10 weeks as T4W1/T4W2.**

**Conclusions**

- Sewage-sludge as a feeding source for soil micro organisms caused the degradation of about 45 to 60% of oil in a polluted soil.
- Hydrocarbon degraders of the heterotrophic bacteria population according to the applied nutrition treatments in this survey had a remarkable increase from $6 \times 10^3$ colony in unit/gr soil in the control sample increased to $2 \times 10^{10}$ in sewage sludge treatments sample.
- C/N ratio 6 in control sample decreased to about 3 in sewage sludge treatments.
- Oil-degradation and microbe population increased in the treatments in the 5 week rather than the 10 week.

**References**

Espinoza YR, Dendooven L (2003) Dynamics of carbon, nitrogen and hydrocarbons in diesel-contaminated soil amended with biosolids and maize. *Journal of Chemosphere* **54**, 379-386.

Gogoi BK, Dutta NN, Krishnamohn TR (2003) A case study of bioremediation of petroleum-hydrocarbon contaminated soil at a crude oil spill site. *Journal of Advance in Environment Research* **7**, 767-782.

Lee Kim SH, S, Kim DY, Kim JG (2007) Degradation characteristic of waste lubricants under different nutrient condition. *Journal of Hazardous Material* **143**, 65-72.

Namkoong W, Hwang EY, Park JS, Choi JY (2002) Bioremediation of diesel-contaminated soil with composting. *Journal of Environmental Pollution* **119**, 23-310.

Ramsay AM, PJ Swannell Warren, Duke A Sh, T. Hill, R. 2000. Effect of bioremediation on the microbial community in oiled mangrove sediments. *Journal of Marian Pollution* **41**, 413-419.

# Comparison of in situ trace element concentration of soil water with concentration in aqueous extracts as a background concentration level

Levke Godbersen[A]; Jens Utermann[B]; Wilhelmus HM Duijnisveld[B] and Gerald Kuhnt[A]

[A]Institute for Physical Geography and Landscape Ecology, Leibniz University Hannover, Schneiderberg 50, D-30167 Hannover, Email levke.godbersen@bgr.de
[B]Federal Institute for Geosciences and Natural Resources, Stilleweg 2, D-30655 Hannover.

## Abstract

This study compares concentrations of trace elements measured in soil water samples with concentrations determined in batch experiments as a background concentration level. One batch experiment was conducted at a liquid/solid (LS) ratio of 5 L/kg with samples specifically adjusted for ionic strength using $Ca(NO_3)_2$ as the background electrolyte. The other is an aqueous extract at a LS ratio of 2 L/kg. Both batch experiments show similar results in their ability to estimate in situ concentrations. The results illustrate that for most trace elements the concentrations, which are determined in extracts, show statistically significant relations (p-value <0.01) with those measured in in situ soil percolation water. The level of fit measured by $R^2$ increases in the following order Pb, Cr<<As<Cu, Zn, Sb, Mo, V< Cd, Ni, Co. Low concentration levels in situ concentrations were underestimated by both extraction methods and vary about two orders of magnitude around the regression mean.

## Key Words

Batch experiment, liquid/ solid ratio 2 L/kg, background electrolyte $Ca(NO_3)_2$, desorption, risk assessment.

## Introduction

In the upcoming revision to the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) the aqueous extraction at a liquid/solid (LS) ratio of 2 L/kg according to DIN 19529 is suggested to be the reference standard for contaminant related risk assessment. Another method of contaminant related risk assessment in soil and groundwater protection is the model-based soil prediction of contaminant migration, which employs overall substrate sorption isotherms. These isotherms were derived from data gained by batch experiments at a LS ratio of 5 L/kg using $Ca(NO_3)_2$ as the background electrolyte to adapt the natural ionic strength of each sample to compensate for the wider LS. For both extraction methods the same trigger values apply. In addition the German Working Group on water issues (LAWA, 2004) plans to make the trigger values of the soil-groundwater pathway be those with insignificant thresholds (GFS) installed by the German Working Group on water issues (LAWA 2004). The GFS are up to ten times smaller than the trigger values of the BBodSchV. Bearing in mind the natural heterogeneity of the soil and soil parameters, the following questions arise: (1) Is it possible to compare in situ concentrations of trace elements with those measured in solutions from batch experiments? (2) Are there significant differences in the results of the different batch methods? (3) What is the accuracy with which we can estimate trace element concentrations in the soil water by batch experiments at the concentration level of the GFS?

## Methods

The sampling sites were selected to determine regional representative background concentrations of trace elements in soil percolation water. Each pair of samples, liquid and solid phase, has been taken at the transition of the unsaturated to the saturated zone. The sample pairs originate from 37 sites in Northern Germany. The total population consists of 270 sample pairs, where soil sediment and soil water were sampled at exactly the same depth. We took samples from soils of the three major parent material classes of Northern Germany: sand, boulder clay and loess. Within the class of sand we categorized three different groups of land use: arable land, grassland and forest. The samples thus show a wide range of pH values (<3 to >7), particle size distributions and ionic strength (electrical conductivity ranges from <100 µS cm^{-1} to >3000 µS cm^{-1}). The soil water was taken with sorption free suction cups with an internal sample collector at the transition of the unsaturated to the saturated zone (Duijnisveld *et al.* 2008). Table 1 shows the medians and the 25th and 75th percentiles of the trace element concentrations measured in soil percolation water as well as the GFS. The data show that the trace element concentrations are in the same order of magnitude as the GFS.

**Table 1. Median, 25th and 75th percentile of in situ measured trace element concentrations and insignificance thresholds (GFS).**

| Element | N | 25th percentile | Median | 75th percentile | GFS |
|---------|---|-----------------|--------|-----------------|-----|
| | | | µg/L | | |
| As | 158 | 0.35 | 0.50 | 0.91 | 10 |
| Ba | 197 | 30.84 | 44.00 | 63.27 | 340 |
| Cd | 265 | 0.03 | 0.09 | 0.43 | 1 |
| Co | 270 | 0.18 | 0.53 | 3.41 | 8 |
| Cr | 269 | 0.29 | 0.60 | 1.28 | 7 |
| Cu | 269 | 1.20 | 3.00 | 6.80 | 14 |
| Mo | 258 | 0.03 | 0.11 | 0.39 | 35 |
| Ni | 270 | 1.10 | 3.02 | 8.99 | 14 |
| Pb | 207 | 0.13 | 0.32 | 0.92 | 7 |
| Sb | 270 | 0.06 | 0.14 | 0.33 | 5 |
| V | 265 | 0.16 | 0.41 | 2.18 | 4 |
| Zn | 240 | 4.13 | 14.09 | 70.35 | 58 |

Trace element concentrations were analysed using inductively coupled plasma mass spectrometry (ICP-MS). The properties pH and electrical conductivity (EC) were analysed on site for the liquid samples. The pH of the soil sample was measured both in $H_2O$ and $CaCl_2$, and EC was measured in an aqueous (LS ratio 5 L/kg) extract (results not shown). The aqueous extraction at a LS ratio of 2 L/kg was conducted according to DIN 19529 with an equilibrium time of 24 h. The mixtures were shaken in an end-over-end shaker at 4-5 rpm. For the extraction at a LS ratio of 5 L/kg the EC of the liquid reagent was adjusted using $Ca(NO_3)_2$ as the background electrolyte and it was adjusted to the EC measured in the corresponding soil water sample. The mixture was shaken for 48 h at 20 rpm (Heidkamp, 2005; Utermann *et al.* 2005). Both kinds of extracts were centrifuged before filtration and being stabilized by acidifying the filtrate with 1% $HNO_3$ for trace element analysis in the ICP-MS. In the remaining supernatant we measured pH and EC of each sample. Due to the $log_{10}$-normal distribution of the data, regression analysis has been calculated with $log_{10}$-transformed data.

### Results

For most elements regression analysis showed statistically significant, and more or less distinct relationships, between trace element concentrations measured in soil water and in extracts. Table 2 shows the regression coefficients of both comparisons. Only Pb concentrations in the LS ratio 2 L/kg extract showed no statistically significant relationship to its in situ response. Pb is known to be hardly soluble in aqueous solutions. Also the coefficient of determination for the relationship in situ vs. LS 5 L/kg of $R^2 = 0.37$ does not allow inference at a higher level of accuracy. Even poorer results, although statistically significant, were calculated for Cr.

The $R^2$ increased in the following order for comparison of in situ vs. LS 2 L/kg: Pb, Cr<<As<Cu, Ni, Zn, Co, Sb, Mo, V< Cd. The order slightly changes for the relation between trace elements determined in situ and in LS 5 L/kg extracts: Cr<< Sb, As, Pb< Cu, Mo < Zn, V, Cd < Ni, Co. These results are in good agreement with the order of mobility of the trace elements (Brümmer *et al.* 1986). The highest regression coefficients show that no more than 60-70% of response variation of the in situ determined trace element concentration can be "explained" by the concentrations measured in the extracts (Table 2). Table 2 also shows that the $R^2$ in the regressions with the trace element concentrations measured in LS 5 L/kg are slightly higher. This may be mainly due to methodological artefacts, such as the well fitted ionic strength (EC $R^2=0.99$), different velocities of end-over-end shaking or the longer equilibrium time of 48 h instead of 24 h.

**Table 2. Adjusted regression coefficients with p-value<0.01 for the relationship between pH, EC or trace element concentrations measured in situ and in extracts of LS ratios of either 2 L/kg or 5 L/kg.**

| | | pH | EC | As | Cd | Co | Cr | Cu | Mo | Ni | Pb | Sb | V | Zn |
|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|
| R² adj | in situ~ LS 2 L/kg | 0.67 | 0.36 | 0.34 | 0.5 | 0.45 | 0.04 | 0.4 | 0.46 | 0.43 | - | 0.46 | 0.46 | 0.45 |
| R² adj | in situ ~ LS 5 L/kg | 0.73 | 0.99 | 0.37 | 0.58 | 0.63 | 0.18 | 0.42 | 0.47 | 0.62 | 0.37 | 0.36 | 0.59 | 0.57 |

Figure 1 shows that the variance of the data is about one order of magnitude higher or lower than the regression mean. This variation can be caused by various effects. Soil as a part of the natural environment is exposed to several influences while developing, and, therefore, is a heterogeneous compartment. Drying and re-moistening the soil samples may influence the solubility of the trace elements, as well as aging effects due to different storing times (Strawn, 1999 in Selim, 1999; Jones and Edwards, 1993). The variation between the pH-value in situ measured and in extracts, which is also apparent in the moderate $R^2$ (Table 1), may also contribute to a varying solubility.
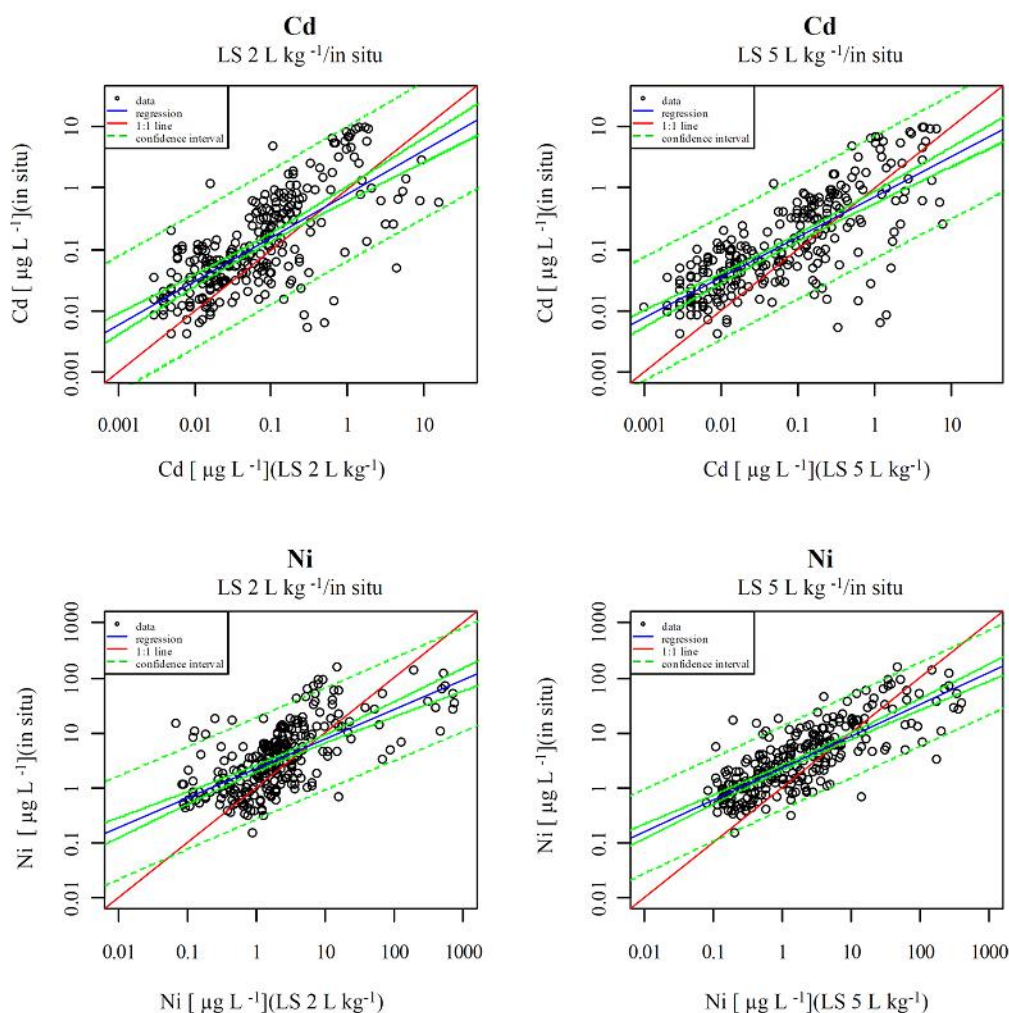


**Figure 1. Regression plots of Cd and Ni concentrations in extracts related to corresponding in situ concentrations in soil percolation water (○ = data, red line = 1:1 line, blue line =regression, dashed green lines = confidence interval).**

As expected, especially at lower concentration levels, the in situ trace element concentrations are underestimated by the concentration measured in the extracts. This causes the regression line to deviate from the 1:1 line. The dilution effect is due to the wider LS range than in situ. However, both extracts underestimate the concentrations at a similar level, which shows the effect of ionic strength adjustment.

**Conclusion**
The study shows, in principle, that both batch methods, aqueous extracts with LS ratio 2 L/kg and extracts with adjusted ionic strength at a wider LS ratio of 5 L/kg using $Ca(NO_3)_2$ as a background electrolyte, are equally applicable to estimate in situ concentrations. Both methods of aqueous extraction show similar results. However, the results also show that data gained by batch experiments should primarily be used for exploratory in opposition to detailed risk assessment. Especially at the critical low concentration levels (of GFS), in situ concentrations are underestimated. Thus, the relation between in situ measured concentrations and concentrations measured in extracts is not one-to-one. Additionally, the data from batch experiments exhibit a variance of about two orders of magnitude. In order to confirm statistically exceeded thresholds, in situ concentrations must be at least one order of magnitude higher than the GFS.

**References**

Brümmer G, Gerth J, Herms U (1986) Heavy Metal Species, Mobility and Availability in Soils. *Z. Pflanzenernaehr. Bodenk.* **149**, 382-389.

DIN 19529 (2009) Elution von Feststoffen - Schüttelverfahren zur Untersuchung des Elutionsverfahrens von anorganischen Schadstoffen mit einem Wasser/Feststoffverhältnis von 2l/kg'.

Duijnisveld WHM, Godbersen L, Dilling J, Gäbler HE, Utermann J, Klump G, Scheeder G (2008) Ermittlung flächenrepräsentativer Hintergrundkonzentrationen prioritärer Schadstoffe im Bodensickerwasser. Endbericht UBA-Forschungsvorhaben 204 72 264, 163 pp.

BBodSchV (1999) German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV). Bundesanzeiger, Berlin.

Heidkamp A (2005) Pedotransfer-Funktionen zur Sorption von Schwermetallen in Waldböden. Horizonte-Herrenhäuser Forschungsbeiträge zur Bodenkunde, Band 18. Der andere Verlag, Osnabrück, 169 pp.

Jones DL, Edwards AC (1993) Effect of Moisture Content and Preperation Technique on the Composition of Soil Solution Obtained by Centrifugation. Commun. *Soil Sci. Plant. Anal.* **24**(1&2), 171-186

LAWA (2004) Ableitung von Geringfügigkeitsschwellenwerten für das Grundwasser. Kulturbuch-Verlag, Berlin.

Selim HM, Iskandar IK (1999) Fate and Transport of Heavy Metals in the Vadose Zone, Lewis Publishers, Boca Raton, London, New York, Washington DC.

Utermann J, Meyenburg G, Altfelder S, Gäbler HE, Duijnisveld W, Bahr A, Streck T (2005) Entwicklung eines Verfahrens zur Quantifizierung von Stoffkonzentrationen im Sickerwasser auf der Grundlage chemischer und physikalischer Pedotransferfunktionen. Forschungsbericht zum BMBF-Forschungsvorhaben 02WP0206.

# Degradation pattern of illicit drugs in soil

Raktim Pal[A,B], Mallavarapu Megharaj[A,B], Ravi Naidu[A,B] and Paul Kirkbride[C]

[A]Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095, Email Raktim.Pal@unisa.edu.au and Megharaj.Mallavarapu@unisa.edu.au
[B]CRC for Contamination Assessment and Remediation of the Environment, University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095, Email Ravi.Naidu@crccare.com
[C]Australian Federal Police Forensic and Data Centres, Canberra, Australia, Email paul.kirkbride@afp.gov.au

## Abstract

The abuse of illicit drugs has received worldwide attention due to their significant adverse impacts on human and the environment. The aim of the present work was to determine the degradation pattern of certain compounds (associated with the clandestine manufacture of illicit drugs) in soil. The target compounds include parent drug (methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA)), precursors (pseudoephedrine), and by-products (1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene). The environmental fate of the target compounds were evaluated in three different South Australian soils under non-sterile and sterile conditions. The results of the degradation study indicated that 1-benzyl-3-methylnaphthalene, methamphetamine, and N-formylmethylamphetamine persist for a long time in soil, MDMA and pseudoephedrine persist for a moderate time, and 1-(1,4-cyclohexadienyl)-2-methylaminopropane is not persistent. The role of biotic-abiotic soil processes on the degradation of target compounds was also varied significantly for different soils as well as with the progress in incubation period. The degradation of methamphetamine and 1-benzyl-3-methylnaphthalene can be considered as predominantly biotic as no measureable changes in concentrations were recorded in the sterile soils within one year period. The results of the present study revealed that the degradation pattern depends mostly on the soil conditions and the nature of the compound.

## Key Words
Illicit drug, clandestine lab, methamphetamine, ecstasy, MDMA.

## Introduction
Illicit drugs are those whose nonmedical use is prohibited by the international law and mainly belongs to the class of opiates, cocaine, cannabis, amphetamines type substances (ATSs), etc. (Hall *et al.* 2008; UNODC 2007). ATS comprise two groups of compounds: [1] the amphetamines group (e.g., amphetamine, methamphetamine) and [2] ecstasy group (e.g., 3,4-methylenedioxymethamphetamine (MDMA) and analogous compounds) (UNODC, 2008a). Amphetamine group drugs account for more than three-quarters of ATSs (UNODC 2008b) and currently demand the most attention of all the synthetic illicit drugs (EMCDDA 2007). Methamphetamine continues to be the most widely manufactured ATS and accounted for 68% of the amphetamine groups as per 2006 estimate (UNODC 2008a, b). In comparison to the plant based drugs (e.g., heroin, cocaine, cannabis, etc.), methamphetamine is relatively easy to manufacture in clandestine laboratories from commonly available chemicals (Sasaki and Makino 2006). Methamphetamine manufacture is typically located throughout East and South-East Asia, North America and Oceania due to easy availability of precursors and high demand (UNODC 2008a). In Australia, the ATS market is second only to the cannabis market and may continue to grow (ACC "Organized Crime in Australia" 2009). In 2006-07 ATS seizures accounted for 46% by weight of all drugs seized in Australia, a period when 356 clandestine laboratories were detected across Australia (ACC, "Illicit Drug Data Report, 2006-2007" 2008).

Illicit drugs are manufactured through variety of synthetic routes employing different illicit precursors most commonly in small clandestine labs and also in industrialized mega and super laboratories. The chemicals associated with these clandestine drug laboratories are often improperly disposed of in indoor or outdoor drains, directly on the ground, and in water bodies. In most cases, the exact contents of the waste products are unknown. These chemicals may then be exposed to different environmental compartments (i.e., soil, sediments, ground water, surface water, etc) through diverse processes (e.g., sorption, degradation, leaching, surface runoff, etc.). Thus, it is pre-requisite to systematically investigate the environmental behavior of these clandestine lab chemicals to assess the potential risk due to the release of these compounds into the environment. A series of reports have been published from different countries on the presence of illicit drugs in water bodies, but there is no report on the behavior of these compounds in soil.

The present work was conducted to investigate the degradation pattern of selected parent drug (e.g., methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA)), precursors (e.g., pseudoephedrine), and the by-products (e.g., 1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene) in soils.

## Methods

The soils for the present work were collected from the Mawson Lakes, Sturt Gorge, and Waite Campus of South Australia, which are originally urban impacted backyard, bush, and agricultural land, respectively. The three soils were widely varied in terms of organic carbon, clay content, soil texture, pH, and surface area. The results of the present study employing test soils widely varying in their basic physico-chemical properties (Table 1) may be extrapolated to other soils around Australia to predict the behavior of the target compounds. The test soils were scanned for the presence of any target compounds and none were detected.

**Table 1. Basic physico-chemical properties of the test soil.**

| Soil | Short name | pH (1:2.5 $H_2O$) | Electrical conductivity ($\mu S\text{-}cm^{-1}$) | Cation Exchange capacity (meq-100 $g^{-1}$) | Organic carbon (%) | Dissolved Organic carbon ($\mu g\text{-}mL^{-1}$) | Sand (%) | Silt (%) | Clay (%) | Textural class | B.E.T. Surface area ($m^2\text{-}g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| wson Lakes | ML | 8.91 | 159 | 19.24 | 1.11 | 8.71 | 55.0 | 25.0 | 20.0 | Sandy loam | 26.67 |
| turt Gorge | SG | 5.98 | 36 | 6.30 | 2.88 | 5.84 | 60.0 | 25.0 | 15.0 | Sandy loam | 9.36 |
| ite Campus | WC | 5.64 | 965 | 17.42 | 2.26 | 3.90 | 42.5 | 42.5 | 15.0 | Loam | 4.59 |

In the present study, the degradation pattern was investigated at a single spiking level of 100 µg/g, 50% of maximum water holding capacity of soils, and at $25 \pm 2^0C$ temperature for one year period. To avoid any chance of photodegradation, the soils were incubated in dark. 5 g of soil in individual amber colored screw cap vials of 40 mL capacity were spiked with the test compounds. The pre-incubated stabilized soils were used for both the non-sterile and sterile degradation studies. The soils (in individual vials) were sterilized by autoclave for three consecutive days at $121^0C$ for 20 min. The soils for both the non-sterile and sterile degradations were spiked with requisite amount of the freshly prepared stock solution. In case of the sterile degradation, the stock solutions were passed through sterile 0.20 µm filter and soils were spiked aseptically within a laminar air flow.

The analytical technique (including soil extraction, sample clean-up, and analysis involving HPLC-MS and GC-MS) was developed for precise quantification of the test compounds.

## Results

In this work, degradation of the target compounds (e.g., methamphetamine, MDMA, pseudoephedrine, 1-(1,4-cyclohexadienyl)-2-methylaminopropane, N-formylmethylamphetamine, and 1-benzyl-3-methylnaphthalene) was studied both under non-sterile soil conditions (where both biotic and abiotic degradation can take place) and sterile conditions (where only abiotic degradation can take place) in all the three soils. Most of the compounds showed substantial degradation in the sterile soils indicating the possible role of the abiotic factors other than photolysis as the incubation was performed under dark throughout the experimental period. The resistance to degradation in non-sterile soils was found in the following descending order: 1-benzyl-3-methylnaphthalene > methamphetamine > N-formylmethylamphetamine > MDMA > pseudoephedrine > 1-(1,4-cyclohexadienyl)-2-methylaminopropane. The degradation of methamphetamine and 1-benzyl-3-methylnaphthalene showed a fairly steady pattern throughout the incubation period when compared in terms of the residual concentration.

No changes in concentrations of methamphetamine and 1-benzyl-3-methylnaphthalene were apparent in the sterile soils within one year period. MDMA, pseudoephedrine, and N-formylmethylamphetamine, were somewhat less stable while 1-(1,4-cyclohexadienyl)-2-methylaminopropane was very unstable.

The experimental data were fitted to regression equations considering first order reaction. The half-life values were calculated from the best fit lines of the logarithm of residual concentrations vs. time elapsed in the incubation period. The half-life values for the non-sterile degradation were recorded in the following ascending order: 1-(1,4-cyclohexadienyl)-2-methylaminopropane (0.8 to 8.3 days) < pseudoephedrine (3.7 to 30.1 days) < MDMA (15.4 to 59.0 days) < N-formylmethylamphetamine (35.0 to 43.6 days) <

methamphetamine (130.9 to 501.7 days) < 1-benzyl-3-methylnaphthalene (150.5 to 10034.3 days). However, the same for the sterile degradation were found to follow the order: 1-(1,4-cyclohexadienyl)-2-methylaminopropane (2.60 to 5.6 days) < MDMA (75.3 to 107.5 days) < N-formylmethylamphetamine (188.1 to 301.0 days) < pseudoephedrine (143.3 to 501.7 days).

Interestingly, 1-(1,4-cyclohexadienyl)-2-methylaminopropane showed the fastest degradation both under the non-sterile and sterile conditions. In addition, almost a parallel degradation pattern of 1-(1,4-cyclohexadienyl)-2-methylaminopropane both under non-sterile and sterile conditions indicated the dominant role of the soil abiotic factors compared to biotic components.

### Conclusions
The results showed that the overall degradation mostly relies on the role of biotic and/or abiotic factors of individual soil plus the molecular nature of the target compound. Methamphetamine and certain synthetic by-products 1-benzyl-3-methylnaphthalene and N-formylmethylamphetamine recorded long persistence in the test soils which is not desirable and need further study to investigate their long term metabolism pattern and impacts of these compounds on the biota including their bioaccumulation potential.

### References
EMCDDA (European Monitoring Centre for Drugs and Drug Addiction) (2007) Annual Report: The state of the drugs problem in Europe. http://www.emcdda.europa.eu/html.cfm/index44682EN.html [Accessed on September 24, 2008].

Hall W, Degenhardt L, Sindicich N (2008) Illicit drug use and the burden of disease. In 'International encyclopedia of public health'. (Eds. K Heggenhougen, S Quah), pp. 523-530. (Elsevier).

Sasaki T, Makino Y (2006) Effective injection in pulsed splitless mode for impurity profiling of methamphetamine crystal by GC or GC/MS. *Forensic Science International* **160**, 1-10.

UNODC (United Nations Office on Drugs and Crime) (2007) World Drug Report. United Nations publication. http://www.unodc.org/pdf/research/wdr07/WDR_2007.pdf [Accessed on May 1, 2008].

UNODC (United Nations Office on Drugs and Crime) (2008a) World Drug Report. United Nations publication. http://www.unodc.org/documents/wdr/WDR_2008/WDR_2008_eng_web.pdf [Accessed on October 24, 2008].

UNODC (United Nations Office on Drugs and Crime) (2008b) Amphetamines and Ecstasy: Global ATS Assessment. United Nations publication. http://www.unodc.org/documents/scientific/ATS/Global-ATS-Assessment-2008-Web.pdf [Accessed on October 17, 2008].

# Different patterns of organic acid exudation in metallophyte and agricultural plants at increasing copper levels

Sebastián Meier[A], Marysol Alvear[A], Fernando Borie[A], Paula Aguilera[A] and Pablo Cornejo[A,B]

[A]Scientifical and Technological Bioresource Nucleus, BIOREN-UFRO, Universidad de La Frontera, P.O. Box 54-D, Temuco, Chile.
[B]Corresponding autor. Email pcornejo@ufro.cl.

## Abstract

Copper (Cu) accumulation in shoot and root tissues and low molecular weight organic acids (LMWOA) root exudation have been studied in two metallophytes from Central Chile (*Oenothera affinis* and *Imperata condensata*) and two agricultural plants (*Lupinus albus* and *Helianthus annus*) growing under hydroponics conditions at increasing Cu levels (0, 0.125, 0.250, 0.5, 1 and 2 mg Cu/L). The plants were grown in mineral solution for four weeks and after that in Cu-added solution for ten days, harvested and analyzed after this time. All the plant species showed high Cu accumulation, highlighting *O. affinis* with 116 and 2657 mg Cu/kg in shoots and roots, respectively. Strong differences in the LMWOA exudated by the different plant species were determined. *O. affinis* exudated high amounts of succinic acid, while *I. condensata* exuded citric and oxalic acids. Acid root exudations from agricultural plants were mainly composed by citric acid. This result suggests that LMWOA root exudates by metallophytes play an important role against high Cu levels in polluted soils, being an important factor for plant selection in the design and implementation of phytoremediation programs.

## Key Words

Cu tolerance, metallophytes, organic acid exudation, phytoremediation.

## Introduction

The main sources of metals in the environment are anthropogenic, such as agriculture, domestic and industrial wastes and mining, being the latter the more important (Ginocchio *et al.* 2004). Under this environmental stress, some plants have developed diverse mechanisms for tolerating high metal levels such as exudation of low molecular weight organic acids (LMWOA) (Tao *et al.* 2004). These exudates play an important function mobilizing low mobile/soluble nutrients (e.g., P, Fe, Zn), increasing microbial activity and complexing metals thus affecting the metal bioavailability. In this sense, the extracellular metal complexation could be an important adaptative mechanism for plant establishment in nutrient deficient soils or in those polluted with high metal levels (Shen *et al.* 2002).

On the other hand, it has been found that LMWOA are involved in the metal transport and storage in plants (Nigam *et al.* 2001). Under high Cu levels the exudation of LMWOA by agricultural plants has been widely studied, and several reports have shown that roots might exude diverse LMWOA, including citric, oxalic and succinic acid, which could play a important role in alleviating Cu toxicity (Quartacci *et al.* 2009). However, the exudation of LMWOA by plants tolerant to high Cu levels has not been extensively studied. In this way, there are no studies which contrast the Cu tolerance, Cu accumulation and exudation of LMWOA between Cu metallophyte and agricultural plants. Based on the aforementioned we hypothesized that LMWOA exudation may be a crucial Cu tolerance mechanism developed by metallophytes naturally growing in Cu polluted areas.

Therefore, the aim of this work was to determine the exudation pattern of LMWOA in mineral solutions, and Cu concentration of two metallophyte species and to contrast their behavior with two agricultural plants growing in the same conditions, for analyzing its possible use in phytoremediation.

## Methods

### Biological material and culture conditions

Commercial seeds of the agricultural plant species *Helianthus annus* and *Lupinus albus* cv. Rumbo-B, and seeds of *Oenothera affinis* obtained *in situ* in Cu polluted soils were sown. Additionally, stolons of *Imperata condensata* were collected from the polluted area to produce plantlets. The collect area was a Mediterranean ecosystem strongly affected by the deposit of metal-rich particles, located approximately at 1.5 km southeast from the Ventanas smelter (CODELCO), in the Puchuncaví valley, Central Chile (32°46′ 30″ S 71° 28′ 17″

W). All seedlings were grown in perlite/sand/vermiculite substrate (1:1:1, v:v:v), supplemented with sterile ddH$_2$O and maintained in a growth chamber until roots reached > 2 cm-length. Then, the plants were transferred to 1-L polyethylene containers and were continuously aerated by air pumping. The nutrient solution used was 1.3 m$M$ MgSO$_4$, 2.0 m$M$ Ca(NO$_3$)$_2$, 2.0 m$M$ KNO$_3$, 2.0 m$M$ K$_2$HPO$_4$, and (in µ$M$) 0.2 µ$M$ CuSO$_4$, 1.0 µ$M$ ZnSO$_4$, 2.0 µ$M$ MnCl$_2$, 20 µ$M$ H$_3$BO$_3$, 0.1 µ$M$ (NH$_4$)$_6$Mo$_7$O$_{24}$, and 200 µ$M$ FeEDTA. The containers were placed into a plant growth chamber room under controlled conditions. After 4 weeks growing in this culture conditions the nutrient solution was replaced by the same solution described above, but supplied with 0, 0.125, 0.5, 1.0 and 2.0 mg Cu/L as CuSO$_4$ This test solution was replaced every two days to keep constant concentrations of nutrients and Cu. The plants grew in these conditions for 10 days, and after the root exudates were collected using the methodology proposed by Rosas *et al.* (2007) with minor modifications.

*Measurements*
Plants with intact roots were rinsed thoroughly with 50 mL of deionized water ($\leq$ 1 µS/cm) and then were immersed in deionized water under constant aeration for 1 h. The solution was filtered (0.22 µm) and freeze-dried. In order to quantify the concentration of LMWOA the residue was resuspended in 300-500 µL of deionized-sterilised water for HPLC injection. The separation was conducted on a 250 × 4 mm reverse phase column (LiChrospher 100 RP-18 5 mm particle size; Merck, Darmstadt, Germany). Sample solutions (20 µL) were injected onto the column and 200 m$M$ orthophosphoric acid (pH 2.1) was used for isocratic elution, with a flow rate of 1 mL/min and UV detection at 210 nm. Identification of organic acids was performed by comparison of retention times and absorption spectra with standards for each organic acid. After to obtain the root exudates, the plants were cut separating shoot and roots, washed with distilled water, oven-dried at 60 ºC for 48 h and weighed. The tissue samples obtained were crushed and converted into ash in a furnace and digested using a H$_2$O/HCl/HNO$_3$ mixture (8/1/1 v/v/v). The Cu concentrations were determined by Atomic Absorption Spectroscopy (Perkin-Elmer 3110).

**Results**
*Copper accumulation*
All the plant species studied showed Cu concentrations above normal (superior to 20 µg Cu/g DW, Adriano 2001), presenting values between 14 and 40 µg Cu/g DW in shoots, with the exception of *O. affinis* which presented a mean accumulation of 116 µg Cu/g DW at the highest Cu concentration (Figure 1, A). However, the highest differences in Cu concentration were registered in the root, where all species studied showed a sharp increase directly related with the increase in Cu concentration in the solution (Figure 1, B), reaching means of 330-660 µg Cu/g DW in the roots of all species at the highest Cu level, with the exception of *O. affinis* which at the same conditions sowed up to 2660 µg Cu/g (4 times higher than concentration in shoots and roots of the other species evaluated) (Figure 1).

*Root exudates*
Four different LMWOA were detected: succinic acid, oxalic acid, citric acid and small amounts of fumaric acid, which were strictly dependent of the plant species analyzed and the amount of Cu added to the solution (Figure 2). Succinic acid was principally exuded by the metallophyte *O. affinis,* which exuded high amounts at increasing Cu concentration, reaching values of 1048,56 µmol/h DW at the higher Cu level (Figure 2C). On the other hand, *Imperata condensata* exhibited LMWOA exudation rate was very variable under different Cu conditions. At low Cu concentrations (between control treatment and 0.125 mg Cu/L) *I. condensata* showed a low exudation of succinic acid (Figure 2C); however, at increasing Cu concentrations this metallophyte produced large amounts of citric and oxalic acid, reaching values of 164,05 and 1,61 µmol/ h.g DW respectively at the highest Cu concentrations (Figure 2 A, B). Root exudates of *L. albus* and *H. annus* contained exclusively citric acid (Figure 1A), which was exuded in high amounts, reaching on an average of 46,01 and 51,44  mol/h.g DW; however, the concentration of citric acid remained relatively constant with increasing copper concentrations in both plants.
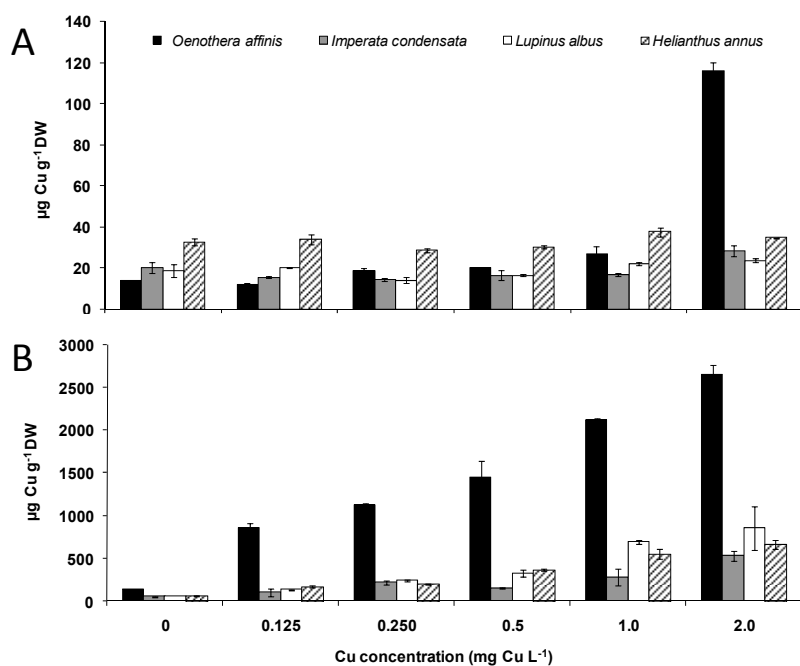
**Figure 1. Copper (Cu) concentration in (A) shoots and (B) roots of four plants species in response to increasing Cu levels (0; 0.12; 0.250, 0.5; 1.0 and 2.0 mg Cu/L). Bars denote means ± S.E (n = 6). DW= Dry weight.**
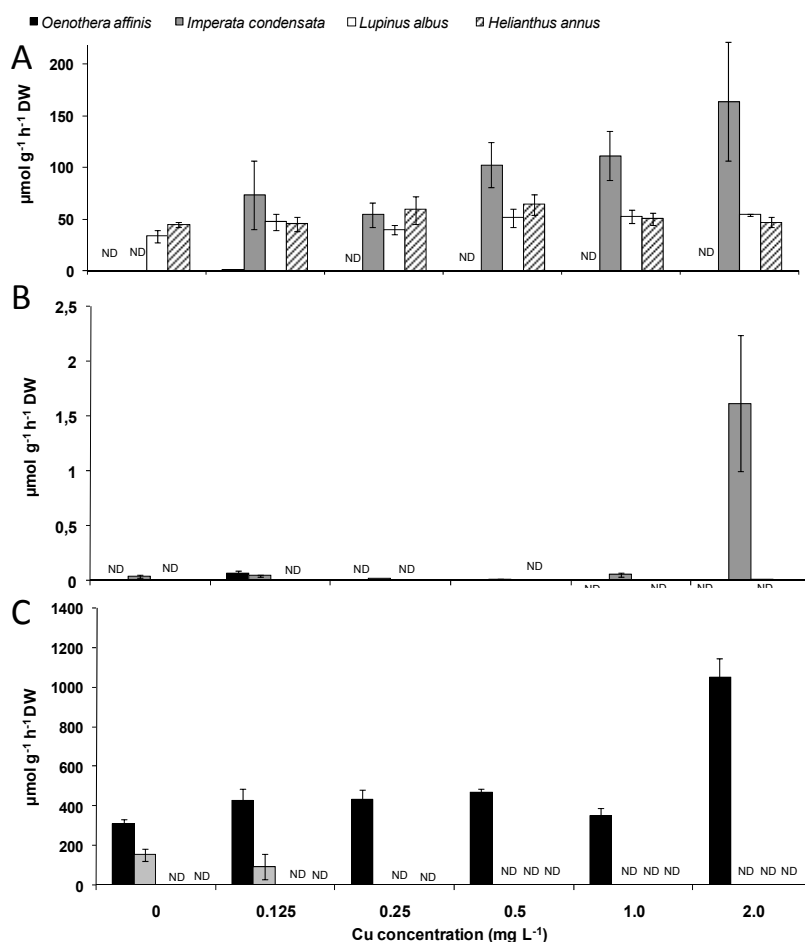


**Figure 2. Exudation of low molecular weight organic acids in four plant species in response to increasing copper levels (0; 0.12; 0.250, 0.5; 1.0 and 2.0 mg Cu/kg). A) Citric acid, B) oxalic acid, C) succinic acid. Bars denote means ± S.E (n = 6). DW= Dry weight, ND= Not detected**.

## Conclusion

These results suggest that the different metallophytes and agricultural plants present differences with respect to its Cu tolerance. If metal tolerance is considered to be manifested as a series of physiological traits (including root elongation, metal uptake and accumulation; Baker and Walker 1990), the most tolerant species would be the metallophyte *O. affinis*, due to its high Cu accumulation capacity. Similarly, the differential exudations of LMWOA by plants, and the large amounts exuded by the metallophytes suggest that this is an important defense mechanism developed to tolerate high Cu concentrations. Further studies aimed to investigate the metal binding properties of each compounds released by roots and the possible involvement of other exudates (phenols) are necessary in order to assess their role in Cu tolerance and accumulating capacity of the metallophytes and agricultural plants as technological tool to be used in potential phytoremediation programs in Cu polluted soils.

## References

Adriano D (2001) Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risk of Metals. Springer-Verlag, New York. 857p.

Baker AJM, Walker PL (1990) Ecophysiology of metal uptake by tolerant plants. In 'Heavy Metal Tolerance in Plants: Evolutionary Aspects'. (Ed AJ Shaw) pp. 155-177. (CRC Press, Boca Raton, FL)

Ginocchio R, Carvallo G, Toro I, Bustamante E, Silva Y, Sepúlveda N (2004) Micro-spatial variation of soil metal pollution and plant recruitment near a copper smelter in Central Chile. *Environmental Pollution* **127**, 343-352.

Nigam R, Srivastava S, Prakash S, Srivastava M (2001) Cadmium mobilization and plant availability: the impact of organic acids commonly exuded from roots. *Plant and Soil* **230**, 107-113

Quartacci M, Irtelli B, Gonnelli C, Gabbrielli R, Navari-Izzo F (2009) Naturally-assisted metal phytoextraction by *Brassica carinata*: Role of root exudates. *Environmental Pollution* **157**, 2697-2703.

Rosas A, Rengel Z, Mora ML (2007) Manganese supply and pH influence growth, carboxylate exudation and peroxidase activity on ryegrass and white clover. *Journal of Plant Nutrition* **30**, 253-270.

Shen H, Yan X, Zhao M, Zheng S, Wang X (2002) Exudation of organic acids in common bean as related to mobilization of aluminum and iron bound phosphates. *Environmental and Experimental Botany* **48**, 1-9.

Tao S, Liu WX, Chen YJ, Xu FL, Dawson RW, Li BG, Cao J, Wang XJ, Hu JY, Fang JY (2004) Evaluation of factors influencing root-induced changes of copper fractionation in rhizosphere of a calcareous soil. *Environmental Pollution* **129**, 5-12.

# Etrace Express: software for risk analysis of trace elements in inorganic fertilizers post application

**Giuliano Marchi**[A], Luiz Roberto Guimarães Guilherme[B], Alexandre Beserra da Silva[A] and Ozanival Dario Dantas da Silva[A]

[A]Embrapa Cerrados, Planaltina, DF, Brazil, Email giuliano.marchi@cpac.embrapa.br
[B]Soil Science Dept., Federal University of Lavras, Lavras, MG, Brazil, Email guilherm@dcs.ufla.br

## Abstract

Trace Elements are generally present in inorganic fertilizers as by-products or contaminants. There are however some trace elements that are plant nutrients and are intentionally included in fertilizer formulations. It is acknowledged that exposure to high levels of trace elements (nutrient or not) could pose a health risk to humans. This risk may be estimated by evaluation models. Thus, this work presents a tool, the software Etrace Express, for easy calculation of Risk Based Concentrations of trace elements in inorganic fertilizers post application, which suggest safe limits for agricultural use. The main purpose of this version was to calculate values of trace element concentrations in inorganic fertilizers that may, flexibly, be used by regulators aiming to protect the human health. Etrace Express was based on a model developed for a document prepared by The Fertilizer Institute (TFI, United States) for the US scenario of fertilizer use, entitled "Health Risk Evaluation of Selected Metals in Inorganic Fertilizers Post Application". RBCs calculated by Etrace Express for the US scenario matched those values presented in TFI's document. We thus used Etrace Express to obtain RBCs for the Brazilian scenario. The advantage of using such software is the easiness of customizing parameters for specific scenarios very rapidly.

## Key Words

Heavy metals, soil contamination, food safety, Delphi platform.

## Introduction

An estimate of risk-based concentrations (RBCs) of trace elements (TE) provided by an industry-commissioned study (TFI 2000) has shown that TE levels in commercial inorganic fertilizers are safe for consumers of farm products in the United States. A RBC is the amount of a TE in a fertilizer that is considered safe or protective of health. RBC calculation involves several parameters for many trace elements. To simplify RBCs calculation we produced the software Etrace Express. The software uses the same methodology proposed to develop the risk based concentration in the TFI study. The methodology is a back-calculation of health risks and is standard for a screening level risk evaluation. The software helped us to assess health risks of TEs in the current scenario of fertilizers use in Brazil (Guilherme and Marchi 2007). Parameters such as application rates, soil accumulation factors, body weight, ingestion rates (crops), and plant uptake factors were adopted from the scientific literature. Data on inorganic fertilizers were taken from industry as well as literature studies. Other parameters, considered non-specific for the Brazilian population, were derived from the USEPA, according to TFI. The results obtained indicate that trace elements do not cause harm to human health when considering post application of inorganic fertilizers in Brazil (based on information for phosphate as well as Zn-carrying fertilizers). This study also suggests that the limits currently established by the Brazilian legislation are safe in terms of health risk assessment. Etrace Express is the second generation among the versions of a package that is still being developed. Delphi 2007 platform was used for programming. The aim of this work was to present the software Etrace Express, a tool for RBCs calculation of trace elements in inorganic fertilizers that can be used as an initial guidance for regulators seeking the protection of human health in the current scenario of fertilizers use in Brazil.

## Methods

*Risk based concentrations (RBCs) for Brazilian fertilizers*
Unit RBCs (normalized RBCs representing 1 percent fraction of nutrient content) were calculated by Etrace Express software to represent Brazilian fertilizers. RBCs were calculated according to the equation 1 (Shown in the last page).

*Screening health evaluation*
The lowest RBC for TE were compared to the maximum concentration of metals of potential concern

---

(MOPCs; e.g. As, Cd, Hg, and Zn). This comparison provided the most health protective estimate of health risk. If the concentration of the MOPC in the fertilizer is below the RBC, there is no health risk. If the concentration of the MOPC in the fertilizer is above the RBC, further evaluation is warranted.

## Results

### Etrace express

Data input are presented in two tabs. In the "Configuration" tab, the user may define parameters about fertilizers and main scenarios. The "Input" tab allows definition of parameters such as those related to exposition pathways. After data were provided for these two tabs, RBC calculations are presented in the "Results" tab. Etrace Express calculated RBCs for the data provided in the TFI report (TFI 2000), presenting identical results to those of the original document. For the Brazilian scenario, the software calculated RBCs (Tables 1 and 2) according to data presented in Guilherme and Marchi (2007).

**Equation 1.**

$$RBC = \frac{TR \text{ or } THI}{SACF * \{AR * 1/FON * [(\frac{ED * EF * IRs * RAFs * CF}{BW * AT} * TOX) + (\frac{ED * EF * SA * AF * ABS}{BW * AT} * TOX) + \frac{TR \text{ or } THI}{(\frac{ED * EF * IRc * RAFc}{AT} * PUF * TOX)]\}}}$$

Where:

| | | |
|---|---|---|
| RBC | = | Risk Based Concentration (mg MOPC/kg product); |
| TR/THI | = | Acceptable Target Risk or Hazard Index (Unitless); |
| AR | = | Application Rate (g/m$^2$-year); |
| FON | = | Fraction of Nutrient (unitless); |
| SACF | = | Soil Accumulation Factor (m$^2$-year/g); |
| ED | = | Exposure Duration (years); |
| EF | = | Exposure Frequency (days/year); |
| BW | = | Body Weight (kg); |
| AT | = | Averaging Time (days); |
| CF | = | Conversion Factor (1X 10$^{-6}$ kg/mg); |
| IRs | = | Ingestion Rate Soil (mg/day); |
| SA | = | Surface Area (cm$^2$/event-day); |
| AF | = | Adherence Factor (mg/cm$^2$); |
| IRc | = | Ingestion Rate Crops (kg/day); |
| RAF | = | Relative Absorption Factor (RAF) (unitless); |
| ABS | = | Dermal Absorption Factor (unitless); |
| PUF | = | Plant Uptake Factor (unitless); and |
| TOX | = | Toxicity Values (mg/kg-day or mg/kg-day $^{-1}$). |

**Table 1. Unitary RBCs for phosphate fertilizer (mg trace elements/kg product for each 1% of P2O5 in the fertilizer product).**

| Scenario | As | Cd | Cr | Co | Cu | Pb | Hg | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Adult | Child | Child | Child | Child | Child | Child | Child | Child | Child | Child | Child |
| Brazil | 2.9 | 5.8 | 81470 | 6389 | 165 | 85 | 0.6 | 216 | 435 | 582 | 10064 | 388 |
| TFI | 4.5 | 23 | 34000 | 3100 | 280 | 73 | 0.9 | 42 | 350 | 120 | 2200 | 1200 |

**Table 2. Unitary RBCs for Zn containing micronutrient fertilizers (mg trace elements/kg product for each 1% of Zn in the fertilizers product).**

| Scenario | As | Cd | Cr | Co | Cu | Pb | Hg | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Adult | Child | Child | Child | Child | Child | Child | Child | Child | Child | Child | Child |
| Brazil | 128 | 351 | 3195903 | 277481 | 6531 | 3818 | 31 | 8575 | 19556 | 23919 | 483249 | 14418 |
| TFI | 38 | 210 | 220000 | 23000 | 1800 | 500 | 6.5 | 300 | 2600 | 800 | 17000 | 8600 |

## Conclusion

The software Etrace Express calculated risk based concentrations using data from the TFI report and from Guilherme and Marchi (2007). RBC results calculated by the software matched those of both works. This means that the software is reliable, and may be used in order to simplify RBC calculations.

**References**

The Fertilizer Institute (2000) 'Health risk evaluation of select metals in inorganic fertilizers post application.' (The Weinberg Group Inc.: Washington). http://aapfco.org/tfiRiskStd.pdf.

Guilherme LRG, Marchi G (2007) 'Metais em fertilizantes inorgânicos: Avaliação de risco à saúde após a aplicação'. (ANDA: São Paulo). http://www.anda.org.br.

# Field-scale assessment of phytoremediation at a former oil tank battery in Bruderheim, Alberta

**James Germida**[A], Lori Phillips[B], Adam Gillespie[A] and Richard Farrell[A]

[A]Department of Soil Science, University of Saskatchewan, Saskatoon, SK, Canada, Email jim.germida@usask.ca
[B]Irving K. Barber School of Arts & Sciences, University of British Columbia Okanagan, Okanagan, BC, Canada.

## Abstract
A 3-yr study to assess the effectiveness of plant-based systems to reduce contaminant levels to environmentally acceptable endpoints (as defined by the Canadian Council of Ministers of the Environment; CCME) was established at a former tank battery near Bruderheim, Alberta. Four treatments (unplanted, unfertilized control; unplanted, fertilized control; a standard cool-season grass/legume mixture; and a locally optimized grass/legume mixture) were compared in a randomized complete block design (n=4). The site was monitored for three years, with soils sampled (0–15 cm and 15-45 cm) at the end of each growing season. Analyses included total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), and CCME PHC-fractions. Plant assessments (species composition, above- and below-ground biomass) also were conducted at the end of each growing season. After three growing seasons, TPH concentrations averaged across the site had been reduced by 62% in the surface and 64% subsurface soils. Reductions in PHC concentrations were generally greater in the plots amended with fertilizer and compost, but were similar in the planted and unplanted plots. Reductions in the F2 (C6-C10) fraction, however, generally occurred more rapidly in the planted treatments. There were no significant differences between the standard and locally optimized plant mixes.

## Key Words
Phytotechnology, plant–assisted bioremediation, enhanced rhizodegradation, petroleum hydrocarbons.

## Introduction
Phytotechnologies involve the plant–assisted bioremediation of organic and inorganic contaminants and are essentially a form of ecological engineering that depends on natural, synergistic relationships among plants, microorganisms and the environment. Since 1998, our research has focused on assessing the effectiveness of phytotechnologies as a means of reducing petroleum hydrocarbon (BTEX, TPH and PAH) concentrations in soils contaminated with weathered oil product. This focus reflects the fact that (i) many types of PHCs are amenable to microbial degradation; (ii) the phytoremediation of organic contaminants often involves enhanced microbial degradation in the rhizosphere; and (iii) there are an estimated 200,000 PHC-contaminated sites in the Prairie provinces alone. Research during the past decade has attempted to assess the utility of plants in a remediation capacity under prevailing Canadian environmental conditions and associated regulatory oversight. The results of this work indicate that to fully exploit and use phytoremediation we need to gain a better understanding of: (i) the pool of phytoremediation species found in Canada; (ii) how phytoremediation operates under unique Canadian climatic conditions; (iii) the mechanisms employed by phytoremediator plants to restore contaminated sites; and (iv) the agronomic requirements needed to maximize phytoremediation as an efficient and cost-effective cleanup technology. So, while there is clear recognition that phytotechnologies have the potential to play an important role in future remediation strategies in Canada, there remains a critical need for 'field performance data' to verify this potential, as well as to assess its limitations and determine appropriate uses of the newly emerging phytotechnologies.

To address this need, field-scale assessments of plant-based bioremediation have been conducted at sites impacted with weathered hydrocarbons in the oil and gas producing regions of Saskatchewan and Alberta. The objective of this study was to assess and demonstrate the utility of phytoremediation as a means of reducing petroleum hydrocarbon levels in oil-contaminated soils to environmentally acceptable endpoints. Here, we describe a 3-yr study established at a former tank battery near Bruderheim, Alberta.

## Methods
*Site description*
A field site was established in Bruderheim, AB in the spring of 2003. The site consisted of oil-impacted soil from a tank battery (formerly at the same location). The experimental design for the Bruderheim site was a

randomized complete block (RCBD) with four treatments replicated four times (see Figure 1). Protocols used to evaluate the effectiveness of the phytotechnology at this site were adapted from those described in the *Phytoremediation of Petroleum Hydrocarbons in Soil Field Study Protocol* developed by the USEPA Remediation Technologies Development Forum (RTDF)–Phytoremediation of Organics Action Team (http://www.rtdf.org/public/phyto/phytodoc.htm).



| **Trt 1:** | unfertilized (gypsum), unplanted |
| **Trt 2:** | fertilized, unplanted |
| **Trt 3:** | fertilized, planted (RTDF mix):  creeping red fescue (60%); yellow sweet clover (25%); perennial ryegrass (15%) |
| **Trt 4:** | fertilized, planted (USK mix):  slender wheatgrass (20%); western wheatgrass (20%); Altai wild rye (20%); red clover (20%), Nuttall's salt-meadow grass (20%) |
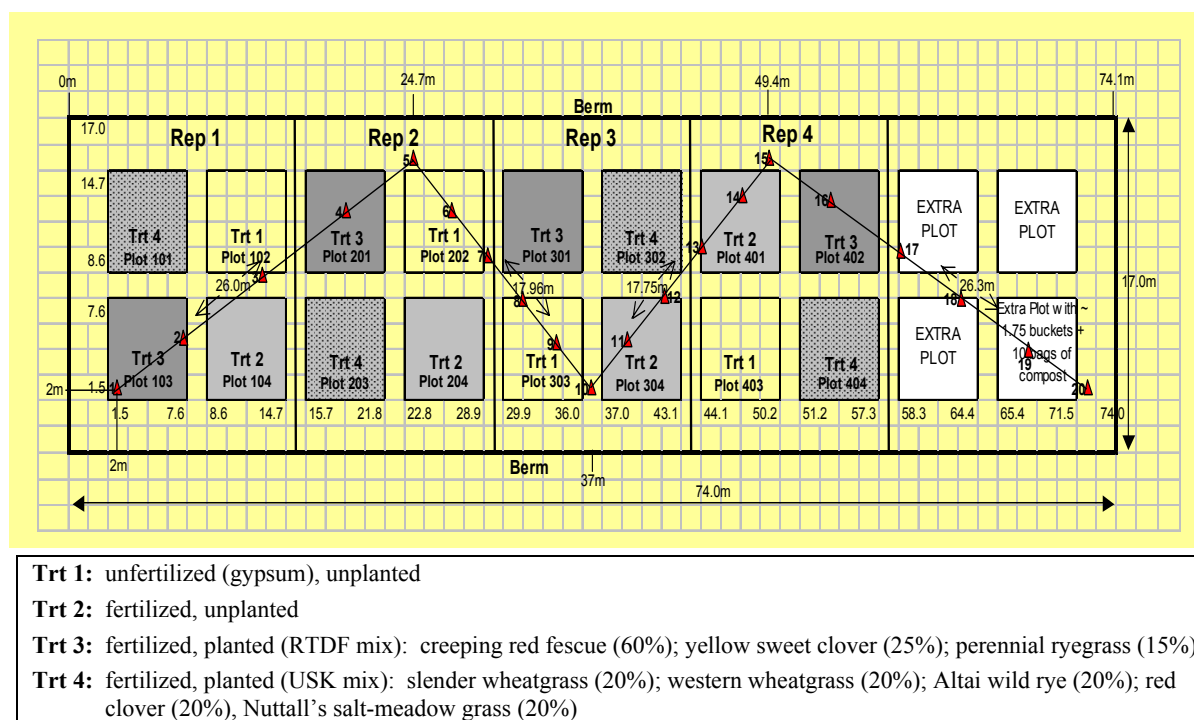
**Figure 1.  Plot plan or the Bruderheim phytoremediation site.**

The site consists of one set (n = 4) of unfertilized/unplanted control plots, one set of fertilized/unplanted control plots, and two sets of fertilized/planted treatment plots. One set of the treatment plots was seeded with a standard (RTDF) plant mix; the second set of treatment plots was seeded with a locally optimized mix of local native/adapted species selected from the plant screening program at the University of Saskatchewan. Individual research plots were 6.1m × 6.1m.

Plots receiving the standard (RTDF) plant mix were seeded with creeping red fescue (47 kg/ha), yellow sweet clover (19 kg/ha), and perennial ryegrass (12 kg/ha). Plots receiving the localized (University of Saskatchewan; USK) plant mix were seeded with slender wheat grass (51 kg/ha), western wheatgrass (130 kg/ha), Altai wild rye (123 kg/ha), red clover (23 kg/ha), and Nuttall's salt meadow grass (19 kg/ha). Because germination rates are generally lower in PHC-contaminated soil than in uncontaminated soil, all plant species were seeded at double the recommended rate.

*Soil sampling and analyses*
Soil characterization and fertility assessments were carried out at the start of the growing season using standard methods (Carter 1993). Plant assessments (percent cover, shoot height, rooting depth & density) were carried out at the end of each growing season, with hydrocarbon analysis of plant tissues being conducted in the last year (i.e., at t3) only. Soil and plant samples were analyzed for PHCs using accelerated solvent extraction (modified EPA Method 3541) followed by analysis for the following target classes: (i) total petroleum hydrocarbons (TPH) by GC-FID (EPA Method 8015); PAHs by GC-MS (EPA Method 8270) ; (ii) CCME PHC-fractions by GC-FID (fractions F1–F4) and GC-MS (fraction F1-BTEX) (Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method; CCME, 2001); and (iii) biomarker steranes and triterpanes (e.g., hopane or norhopane) by GC-MS (modified EPA Method 8270).

A thin-walled, split-core sampler tube fitted with a stainless steel liner was used to collect soil samples. Eight random sub-samples from each treatment plot were combined to make one composite sample per plot.

Replicate (n = 5) samples of each composite soil were packed  into 250-mL wide-mouth, clear-glass jars with Teflon-lined polypropylene lids (e.g., VWR TraceClean™–QA), stored on ice in a cooler, and transported to the University of Saskatchewan where they were placed into a -20°C freezer and stored till they were analyzed using the methods described above.

## Results

*Plant assessments*
Ground cover in the planted treatment plots (Trt. 3 & 4) ranged from about 75-90% at the end of the first growing season (2003), increasing to about 96–99% at the end of the third growing season (2005). Compositional changes in the plant communities were observed in both of the planted treatments. Plots seeded with the RTDF mix (Trt. 3) showed a small but significant increase in percent cover by the creeping red fescue, with a concomitant decrease in percent cover by the perennial ryegrass. Changes in species composition were more noticeable in the plots seeded with the USK mix (Trt. 4), with the slender and western wheatgrasses increasing their coverage–primarily by out-competing the Altai wildrye.

Total above-ground biomass production in both planted treatments was significantly greater during the second season than the first season, though differences between the treatments were generally small. During the third season, the plots were mowed without the knowledge (or consent) of the researchers—resulting in an apparent decrease in total biomass production. Root production in the planted treatment plots generally increased with time, reflecting increases in both plant cover and growth during the second and third growing seasons.

*PHC Degradation*
Initial soil characterization of the Bruderheim site revealed that (i) the TPH concentration in the soil averaged 2148 mg/kg in the surface soil (0-15 cm) and 1939 mg/kg in the subsurface soil (15-45 cm); (ii) BTEX compounds were not present at detectable levels; (iii) concentrations of the F2 (C10-C16) and F3 (C16-C34) PHC-fractions exceeded the Canadian soil quality guidelines (SQG) for a coarse-textured agricultural soil; (iv) naphthalene, phenanthrene and pyrene were the only PAHs detected in the soil, and only phenanthrene and pyrene exceeded the SQG; and (v) the soil was alkaline with a sodium adsorption ratio (SAR) that was slightly greater than the SQG, though the soil was not considered saline. The primary soil chemical indicators used to describe the Bruderheim soil are summarized in Table 1.

Upon completion of the third growing season, TPH concentrations averaged across the site had been reduced to 815 mg/kg in the surface (0-15 cm) soil and 701 mg/kg in the subsurface (15-45 cm) soil. Reductions in PHC concentration were observed in all four CCME fractions, with reductions in the F2 fraction resulting in a final concentration that was 40-60% below than the SQG. Significant reductions also were observed for the F3 fraction, though the final concentration (ca. 500 mg/kg) still exceeded the SQG for a coarse-textured agricultural soil. The change in PHC concentration with time exhibited a similar pattern in all four treatment plots, though reductions in the F2 fraction generally occurred more rapidly in the planted treatments. Reductions in the F4 fraction also were generally greater in the planted treatments.

Reductions in PHC concentrations were generally greater in the plots amended with fertilizer and compost and were slightly greater in the planted plots than in the unplanted plots. Because of the rather high degree of spatial variability associated with the PHC determinations, statistical significance was not observed. Likewise, there were no significant differences between the site-specific (USK) plant mix and the standard (RTDF) plant mix, though this presumably reflects the fact that the RTDF mix consisted of plant varieties that were well adapted to the Bruderheim area. PAH concentrations also decreased significantly after three years (Table 1), and were well below the SQG upon completion of the study.

BTEX compounds were not determined at the final sampling, reflecting the fact that they did not exceed the SQGs at the start of the study. Analysis of a subset of the above-ground biomass from the planted treatments failed to detect any PHCs in the plant tissue. This is in keeping with the vast majority of the published literature, which indicates that plant uptake of PHCs, and most PAHs, during phytoremediation are negligible. As a result, a detailed analysis of the plant tissues was not undertaken.

**Table 1. Primary soil chemical indicators [petroleum hydrocarbons (PHCs), polyaromatic hydrocarbons (PAHs), trace metals, and salinity indices] measured in the surface (0–15 cm) and sub-surface (15–45 cm) soils from the phytoremediation site at Bruderheim, AB. Values in parentheses are the standard deviation from the mean.**

| Soil Parameter | SQG* (mg/kg) | - - - Initial ($t_0$) Conc. - - - (mg/kg) | | - - - Final ($t_3$) Conc. - - - (mg/kg) | |
|---|---|---|---|---|---|
| | | (0–15 cm) | (15–45 cm) | (0–15 cm) | (15–45 cm) |
| **PHCs** | | | | | |
| F1 (C6–C10) | 30 | 1.44 (1.79) | 0.12 (0.29) | 0.03 (0.04) | 0.07 (0.19) |
| F2 (C10–C16) | 150 | 203 (95) | 192 (164) | 89.4 (62.5) | 53.6 (54.7) |
| F3 (C16–C34) | 400 | 1351 (567) | 1369 (589) | 510 (252) | 500 (69.8) |
| F4 (C34–C50) | 2800 | 593 (268) | 378 (189) | 216 (159) | 147 (116) |
| **BTEX** | | | | | |
| Benzene | 0.13 | BDL[†] | BDL | ND[‡] | ND |
| Toluene | 0.16 | BDL | 0.02 | ND | ND |
| Ethylbenzene | 0.36 | BDL | BDL | ND | ND |
| Xylenes | 14 | BDL | 0.01 | ND | ND |
| **PAHs[§]** | | | | | |
| Naphthalene | 0.1 | 0.01 (0.01) | | 0.01 (0.01) | BDL |
| Phenanthrene | 0.1 | 0.14 (0.14) | | 0.01 (0.01) | 0.01 (0.01) |
| Pyrene | 0.1 | 0.26 (0.09) | | BDL | 0.05 (0.02) |
| pH | 6–8 | 8.0 (0.2)[¥] | | 8.0 (0.2) | 8.1 (0.1) |
| EC (ds/m) | 2 | 1.1 (0.5)[¥] | | 0.4 (0.1) | 0.4 (0.1) |
| SAR | 5 | 5.9 (1.1)[¥] | | 3.5 (1.0) | 4.4 (0.8) |

\* Canadian Soil Quality Guideline (CCME, 2004 Update): Land use = agricultural; Soil texture = coarse-grained.
[†] Below detection limit.
[‡] Not determined.
[§] No other priority PAHs were present in the soil.
[¥] Composite sample for the 0–45 cm depth.

## Conclusion

Significant ($P \leq 0.10$) reductions in TPH and the CCME PHC-fractions were observed during the three years of field trials at the Husky Energy site near Bruderheim, AB. Reductions in the F2 (C10-C16) fraction, phenanthrene and pyrene brought the final concentrations of these compounds to levels below those identified in the Canadian Soil Quality Guidelines as needing further remedial action. Despite significant (*ca.* 62%) reductions in the F3 (C16-C34) fraction, final concentrations of this fraction still exceeded the SQG for a coarse-textured agricultural soil. PHC reductions in the planted and unplanted treatments were generally similar. These results notwithstanding, plant establishment provides the additional benefits of enhanced soil stabilization and erosion and runoff control.

## References

Canadian Council of Ministers of the Environment Inc. (2001) Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method. CCME Publication No. 1310. http://www.ccme.ca/ourwork/soil.html?category_id=43.

Canadian Council of Ministers of the Environment Inc. (2004) Canada-Wide Standards for Petroleum Hydrocarbons (PHC) in Soil. http://www.ccme.ca/assets/pdf/phc_standard_1.0_e.pdf.

Carter, MR (1993) Soil Sampling and Methods of Analysis, First Edition. (Lewis Publishers and CRC Press: Boca Raton, FL).

# Gold phytomining in arid and semiarid soils

**Victor Wilson-Corral**[A, B, C], Mayra Rodriguez-Lopez[B, C], Joel Lopez-Perez[B, C], Miguel Arenas-Vargas[B, C, D] and Christopher Anderson[E]

[A]Facultad de Ingeniería-Culiacán, Universidad Autónoma de Sinaloa (UAS), Ciudad   Universitaria, Culiacán, Sinaloa, México C. P. 80040. Email vimawc@uas.uasnet.mx
[B]Centro de Estudios Justo Sierra (CEJUS), Surutato, Badiraguato, Sinaloa, México
[C]Centro de Innovación y Desarrollo Educativo (CIDE A.C.), Col. Ejidal, Guasave, Sinaloa, México. C.P. 80600
[D]Universidad Autónoma Metropolitana-Unidad Xochimilco, Calzada del Hueso 1100, Colonia Villa Quietud, Delegación Coyoacán, México, D.F. C. P. 04960
[E]Institute of Natural Resources, Massey University, Palmerston North, New Zealand.

## Abstract
Metals such as gold, copper and lead can be found in soil at high concentration at many desert locations. However, adverse weather conditions, specifically a lack of moisture, limit the range of applicable technologies to recover these metals. A number of plant species have been tested under both laboratory and field conditions to determine their potential for use in the phytoextraction of metals such as gold. Recorded gold extraction and dry matter yields suggest that phytomining in arid and semiarid zones might be viable if plant species are used that can to adjust to the conditions of these regions.

## Key Words
Induced hyperaccumulation, hyperaccumulator plants, mine tailings.

## Introduction
Environmental conditions such as weather and humidity limit the practice of activities that generate the livelihoods necessary for the survival of desert communities. One of the economic activities that has developed in desert regions is mining. This activity has been conducted in desert regions for centuries (Grattan *et al.* 2004). Various metals such as gold, copper, lead are hosted in desert sites around the globe. The enduring adverse climates (Kondos 2009) and other conditions that prevail in arid and semiarid desert regions often limit the application of appropriate technologies for metal recovery. Despite the limitations, mining activities for certain metals (particularly copper) have developed in some desert areas on an immense scale (Grattan *et al.* 2004). Recent studies reveal the existence of areas of gold mineralization in desert areas around the world (Reid *et al.* 2009). The same conclusion can be made for lead and chromium (Pyatt *et al.* 1999).  These arid-zone mineral deposits could be exploited through application of appropriate mining technologies.

*Induced hyperaccumulation of gold in plants*
Since the early of 20th century, there have been reports about the accumulation of gold by plants, particularly trees (Warren and Delavault 1950). These studies showed that coniferous trees can accumulate quantities of gold that are in the order of parts per billion in their tissues (Warren and Delavault 1950). Some mining companies use plant species as bioindicators of the presence of gold in soil. However, no plant species have been identified that can hyperaccumulate gold naturally. Gold, under natural conditions, is highly insoluble. This reduces its bioavailability and thus limits the potential for phytoextraction; bioavailability is one of the most critical factors for plant uptake of metals (Gardea-Torresdey *et al.* 2005). Scientists have suggested procedures to force hyperaccumulation by applying chemical compounds that promote metal solubility to the substrate of a growing plant. This technique is known as induced hyperaccumulation and provides the basis for the development of phytomining, which is a novel extraction technique to exploit precious metal resources from soil. Phytomining is the use of live plants to recover valuable metals from waste mining substrates (tailings) or mineralized soils. Phytomining has been applied to areas where the metal concentration is not suitable for viable extraction using conventional technologies (Anderson *et al.* 1998). In 1994, scientists conducted the first field trials of induced hyperaccumulation for lead using maize (*Zea mays* L.) and other species (Huang and Cunningham 1996). More recent studies have shown that thallium and nickel are metals for which phytomining may also be economically viable using natural or non-induced hyperaccumulation (Robinson *et al.* 2009).

*Laboratory trial for gold phytoextraction*
In 1998, Anderson and his research group in New Zealand reported, for the first time, results describing the induced hyperaccumulation of gold in plants (Anderson *et al.* 1998). In this work, Indian mustard (*Brassica juncea* Czern.) was induced to accumulate gold concentrations in leaf tissues as high as 57 mg/kg of dry matter (Anderson *et al.* 1998).

Experiments to extract gold from hydroponic solutions using the species *Medicago sativa* L., were published in 1998 and 2002 (Gardea-Torresdey *et al.* 2002). In these reports, thiourea was used to induce gold hyperaccumulation. The data showed that the species could be used for the phytoextraction of gold particles dissolved in hydroponic solutions. In subsequent studies, laboratory tests using the crop plants radish (*Raphanus sativus* L.), onions (*Alluim cepa* L.), beet (*Beta vulgaris* L.) and carrot (*Daucus carota* L.) cultivated in a silica sand containing 3.8 mg/kg gold showed that gold concentrations greater than 200 mg/kg of plant tissue could be achieved (Msuya *et al.* 2000).

In 2005, a study was published in which the species *Chilopsis linearis* Cav. that grows in the deserts of Chihuahua, Mexico, was used to extract gold particles from hydroponic solutions. The results showed the viability of this species to be used in the absorption of gold using ammonium thiocyanate to increase the solubility of metallic gold (Gardea-Torresdey *et al.* 2005).

In 2007 a study conducted in Australia was reported in which the following plant species were tested for gold phytomining: *Eucalyptus polybractea* R.T.Baker (Blue Mallee), *Acacia decurrens* Willd. (Black Wattle), *Sorghum bicolor* L. Moench. (Sorghum) *Trifolium repens* L. (White clover cvs. Tribute and Prestige), *Bothriochloa macra* (Steud) S.T.Blake (Red grass), *Austrodanthonia caespitosa* (Gaudich.) H.P.Linder (Wallaby grass) and *Microlaena stipoides* (Labill.) R.Br. (Weeping grass). The reported results showed that *Trifolium repens* L. *cv*. Prestige could be induced to accumulate gold concentrations higher than 27 mg/kg of dry matter, when cultivated on mine tailings and where sodium cyanide was used as the inducing agent (Piccinin *et al.* 2007).

*Greenhouse trial for gold phytoextraction*
During 2006 studies were conducted in Mexico where plants were tested for their ability to extract gold from spiked sand. In this work the following species were used: *Amaranthus spp* (amaranth), *Sorghum halepense* L. Pers. (Johnson grass), *Helianthus annuus* L. (Sunflower), *Sesamum indicum* L. (Sesame), *Gossypium hirsutum* Tod. (Cotton), *Brassica campestris* L. (Indian mustard) and *Amoreuxia palmatifida* Moc. & Sessé ex DC. (Mexican yellowshow) (Wilson-Corral 2008). Results showed that it is possible to induce gold concentrations above 304 mg/kg of dry matter in *B. campestris* growing in gold-enriched silica sand and using ammonium thiocyanate as the inducing agent for gold hyperaccumulation.

In early 2008, a trial was performed in order to evaluate the gold extraction potential of *Sorghum halepense* L. Pers. cultivated on mine tailings in a greenhouse. Sodium cyanide, thiourea, ammonium thiocyanate and ammonium thiosulfate were used to induce gold hyperaccumulation. These trials revealed that sodium cyanide could induce gold concentrations up to 23.9 mg/kg of dry matter (Rodriguez-Lopez *et al.* 2009a).

During 2009, a test was conducted in which the species *Kalanchoe serrata* Mannoni & Boiteau was grown. This species can grow in high temperature and scarce water conditions that can prevail in deserts (Rodriguez-Lopez *et al.* 2009b). This study revealed that, through application of sodium cyanide to the growing media, it is possible to induce a gold concentrations higher that 9 mg/kg of dry matter in this species.

*Field trials for gold phytoextraction*
During 2003 the first field trial for gold phytoextraction from mine tailings was conducted using sodium cyanide and ammonium thiocyanate as chemicals to induce gold hyperaccumulation (Anderson *et al.* 2005). In this work B*rassica juncea* Czern. (Indian mustard) and *Zea mays* L. (maize) were used to recover gold from rock with a gold concentration of 0.6 mg/kg. The results showed that it is possible to achieve a gold concentration of up to 39 mg/kg of dry matter in Indian mustard under field conditions. This trial showed that potentially between 10 and 20% of the gold present in the substrate can be removed in any one crop.

Towards the end of 2006, researchers at the Centro de Innovacion y Desarrollo Educativo (CIDE AC) conducted field trials in Mexico where plants of *Brassica juncea* Czern. were cultivated in mine tailings. The results showed that it was possible to obtain biomass yields in excess of 8 ton/ha under field conditions (Wilson-Corral, 2008). Finally, in 2009, a field trial was conducted to establish the potential of the species *Helianthus annuus* L. to recover gold from mine tailings. A plot of 50 m$^2$ was constructed. The average gold concentrations for leaves, stems, and roots, were 16, 21, and 15 mg/kg of dry mater, respectively after cyanide treatment of the mature biomass (unpublished).

*Technical assessments*
Scientists at the University of Sydney have evaluated the technical feasibility and the economic viability of nickel and gold phytomining in Australia. In this work possible sites were identified and plant species most suited to these regions and methods of recovering the metals from the plants were suggested. The indicative profitability for a Ni phytomine in Australia was predicted to be 11,500 AU$/ha/harvest, using the hyperaccumulator *Berkheya coddii* Roessler on nickel rich serpentine soils and with energy generation from the harvested biomass. For Au, a profit of 26,000 AU$/ha/harvest was predicted using induced accumulation (with thiocyanate) with a crop of *Brassica juncea* L. coupled with energy generation from the harvested biomass (Harris *et al.* 2009).

**Conclusions**
Tests are ongoing in Mexico under both greenhouse and field conditions to assess the economic returns that could be generated by the implementation of phytomining to extract gold from waste produced by mining activities in this country. Considering the scientific studies reported in this manuscript, the following objectives are being actively researched: a) systems to evaluate the potential of ore, tailings or waste produced by mining activities in arid and semiarid regions for gold phytomining; b) tests to identify plant species that can be used in these areas for gold phytomining; c) economic assessment to determine potential profits that could be gained through applying the technology in arid and semiarid regions; and d) the implementation of commercial scale phytomining operations.

**Acknowledgments**

**References**
Anderson C, Brooks RR, Stewart RB, Simcock R (1998) Harvesting a crop of gold in plants. N*ature* **395**, 553-554.

Anderson C, Moreno F, Meech J (2005) A field demonstration of gold phytoextraction technology. *Minerals Engineering* **18**, 385-392.

Gardea-Torresdey JL, Parsons JG, Gomez E, Peralta-Videa J, Troiani HE, Santiago P, Jose-Yacaman M (2002) Formation and growth of Au nanoparticles inside live alfalfa plants. *Nano Letters* **2**, 397-401.

Gardea-Torresdey JL, Rodriguez E, Parsons JG, Peralta-Videa JR, Meitzner G, Cruz-Jimenez G (2005) Use of ICP and XAS to determine the enhancement of gold phytoextraction by *Chilopsis linearis* using thiocyanate as a complexing agent. *Analytical and Bioanalytical Chemistry* **382**, 347-352.

Grattan JP, Gillmore GK, Gilbertson DD, Pyatt FB, Huntf CO, McLareng SJ, Phillips PS, Denman A (2004) Radon and 'King Solomon's Miners': Faynan Orefield, Jordanian Desert. *The Science of the Total Environment* **319**, 99-113.

Harris AT, Naidoo K, Nokes J, Walker T, Orton F (2009) Indicative assessment of the feasibility of Ni and Au phytomining in Australi. *Journal of Cleaner Production* **17**, 194-200.

Huang BJ, Cunningham (1996) Lead Phytoextraction: species variation in lead uptake and translocation. *New Phytologist* **134**, 75-84.

Kondos P (2009) Gold Extraction: Practices and Challenges. *In* ' 5ta International Conference: Science, Technology and Applications of Gold '. Hiedelberg, Germnay. (Ed. H University), p. 31. (World Gold Council (WGC)).

Msuya FA, Brooks RR, Anderson C (2000) Chemically-induced uptake of gold by root crops: Its significance for phytomining. *Gold Bulletin* **33**, 134-137.

Piccinin RCR, Ebbs SD, Reichman SM, Kolev SD, Woodrow IE, Baker AJM (2007) A screen of some native Australian flora and exotic agricultural species for their potential application in cyanide-induced phytoextraction of gold. *Minerals Engineering* **20**, 1327-1330.

Pyatt FB, Barker GW, Birch P, Gilbertson DD, Grattan JP, Mattingly DJ (1999) King Solomon's Miners Starvation and Bioaccumulation? An Environmental Archaeological Investigation in Southern Jordan. *Ecotoxicology and Environmental Safety* **43**, 305-308

Reid N, Hill SM, Lewis DM (2009) Biogeochemical expression of buried gold mineralization in semi-arid northern Australia: Penetration of transported cover at the Titania Gold Prospect, Tanami Desert, Australia. *Geochemistry: Exploration, Environment, Analysis* **9**, 267-273.

Robinson BH, Banuelos B, Conesa HM, Evangelou MWH, Schulin R (2009) The Phytomanagement of Trace Elements in Soil. *Critical Reviews in Plant Science* **28**, 240-266.

Rodriguez-Lopez M, Wilson-Corral V, Anderson C, Lopez-Perez J (2009a) Chemically Assisted Gold phytoextraction in *Sorghum halepense*. *In* '5ta International Conference: Science, Technology and Applications of Gold '. Heidelberg, Germany. (Ed. Heidelberg University), p. 353. World Gold Council.

Rodriguez-Lopez M, Wilson-Corral V, Lopez-Perez J, Arenas-Vargas M, Anderson C (2009b) Aplicacion Potencial de *Kalanchoe serrata* en Tecnologías de Mineria Ambientalmente Sostenibles In 'Primer Congreso Internacional de Ciencias de la Ingeniería'. Los Mochis, Sinaloa. (Ed. CP Barrios Durstewitz) pp. xxx-xxx. (Universidad Autonoma de Sinaloa).

Warren HV, Delavault RE (1950) Gold and silver content of some trees and horsetails in British Columbia. *Geological Society of America Bulletin* **61**, 123-128.

Wilson-Corral V (2008) Hiperacumulación de oro inducida químicamente en ocho especies vegetales (*Brassica juncea, Brassica campestris, Helianthus annus, Amaranthus spp., Sesamum indicum, Sorghum halepense, Amoreuxia palmatifida y Gossypium hirsutum*). PhD Thesis. Centro de Estudios Justo Sierra (CEJUS).

# Heavy metals distribution in soil particle size fractions from a mining area in the southeast of Spain

Silvia Martínez-Martínez[A], Ángel Faz[A,C], Jose A. Acosta[A,B], Dora M. Carmona, Raúl Zornoza, Asuman BüYükkiliç[A] and Sebla Kabas [A]

[A]Sustainable Use, Management, and Reclamation of Soil and Water Research Group. Department of Agrarian Science and Technology. Technical University of Cartagena. Paseo Alfonso XIII, 52, 30203 Cartagena. Murcia. Spain.
[B]Institute for Biodiversity and Ecosystem Dynamics. University of Amsterdam. Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.
[C]Corresponding author. Email angel.fazcano@upct.es

## Abstract

The distribution of heavy metals in soil particle size fractions from soils on two representative tailing ponds, El Lirio and El Gorguel, from the southeast of Spain has been studied. In both tailing ponds heavy metal mobility is not enhanced owing to the high pH despite a low buffer capacity. In addition, the materials showed a low fertility and high salinity, which prevent plant colonization and leave their surface unprotected against wind and water erosion. The dominant fraction for both ponds was 425–150 μm, while the finest fraction represented 23 % and 20 % for Gorguel and Lirio tailing ponds, respectively.  High concentration of metals occurred in both finest and coarsest fractions due to high surface area and negative charges associated with fine particles and the processes of treatment of the ore. The results showed high pollution of these ponds for all the fractions. However, highest enrichment factors (EFs) were in the finest (<75 μm) and coarsest (2000-425 μm) particles with EFs >10 for Pb; >15 for Cd and >20 for Zn in Lirio and EFs>10 for Pb; >20 for Cd and >30 for Zn in Gorguel.

## Key Words

Tailing pond, heavy metals, particle size, mining activities.

## Introduction

In Murcia Province, there are 85 mining tailing ponds due to intensive mining activities that occurred during the last century, especially in the Sierra de Cartagena-Union. Although mining activity was abandoned several decades ago, those tailing ponds with high amount of heavy metals still remain in the area. The tailing ponds, due to their composition and location, may create environmental risks of geochemical pollution, negatively affecting soil, water, plant, animal, and human populations, as well as infrastructure. As most of these ponds are not covered by vegetation or any other material, wind and water erode their surface and high amount of material is transported long distances, especially fine particles.  Fine particles have high specific area that retains high amounts of metals (Wang *et al.* 2006). In addition, small particles are often soluble and metals are more likely to traverse the gastric mucosa and be more efficiently adsorbed in human tissues than for coarse fractions (Lin *et al.* 1998).  The objective of the present study is to evaluate the effect of particle size on the distribution of heavy metals in tailing ponds from a mining area in Southeast Spain.

## Methods

### Study area and sampling

Mine tailings are located in the Murcia Province (Spain) Cartagena-La Unión Mining District, where much mining activity had been carried out for more than 2500 years, stopping in the nineties.
The climate of the area is a typical Mediterranean with mean monthly temperature of 9.3 °C in January to 24.4 °C in July. Total annual rainfall varies between 279 and 406 mm with on average ~ 275 mm, in autumn and spring.  The potential evapo-transpiration rate surpasses 900 mm/y.  Two tailing ponds generated by mining activities were selected, El Lirio and El Gorguel. These ponds are representative of existing ponds in Sierra Minera de Cartagena-La Unión, with similar problems and characteristics. The selection of these two ponds was based on access, physico-chemical characteristics (based on previous studies), hydrological conditions, slope, distance from towns, surrounding landscape, etc.  Surface soil samples were collected according to a regular sampling grid of 100 m$^2$ using a Geographic Information System - GIS. Aerial orthophotos were used to design the grid so that sampling was representative of the surface area topography of each pond (Figure 1).
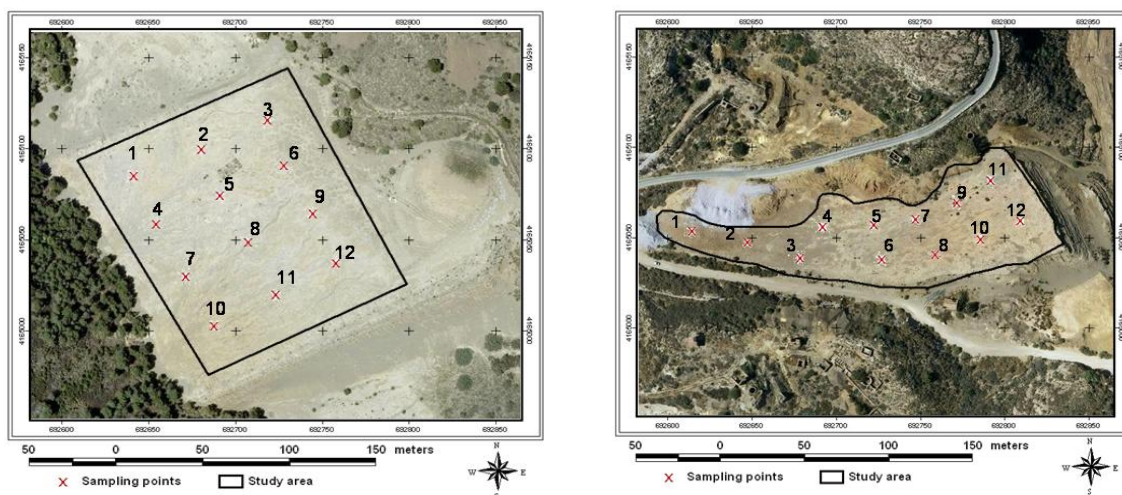
**Figure 1. Design of soil surface sampling grids for El Lirio (left) and El Gorguel (right) tailing ponds.**

*Analytical methods*

For the physico-chemical characterization of the surface soil at the two ponds, a sampling was carried out in April 2009 according to the designed sampling grids. Samples were taken from the soil surface (0-15 cm). The collected samples were taken to the lab, air-dried for 7 days, passed through a 2-mm sieve, homogenized, and stored in plastic bags at room temperature prior to laboratory analyses.

The analyses for this study were determined as follow: pH measured in a 1:1 water soil ratio solution according to Peech´s method (1965); soluble salts according to Bower and Wilcox (1965); organic carbon and nitrogen according to Duchaufour (1970), cation exchange capacity following the method of Chapman (1965), particle size analysis carried out by using the FAO-ISRIC system (1990) using a combination of pipette and sieving. The fractionation of bulk soils into five particle size fractions was conducted using sieves with the following sizes: 2000, 425, 150, 106 and 75 μm. For the quantification of the total metals in each fraction, a subset of each particle size fraction was ground, and an acid digestion (nitric-perchloric) was used (Risser and Baker 1990) (210 ºC during 1:3 h and with addition of 0.1 N HCl). Measurement of metals was carried out using atomic an absorption spectrophotometer (AAnalyst 800, Perkin Elmer). We interpritated the amount of metal in the mine waste using an enrichment factor, calculated with respect to highest limit concentration allowed by European regulations (Banat *et al.* 2005; Madrid *et al.* 2002; Chan *et al.* 2001).

## Results

*Physico-chemical characterization*

Mean values of pH in the tailing ponds were 5.39 and 7.41 for Lirio and Gorguel respectively, thus heavy metal mobility is not enhanced at these pH values, although a higher mobility is expected in El Lirio. Additionally, no carbonate was detected for both ponds, indicating that the buffer capacity of these residues is low. Similar contents for organic carbon (O.C.) and total nitrogen (T.N.) were found in both mining ponds, with mean values of 0.37 and 0.42 % O.C. and 0.01 and 0.02 % T.N. for Lirio and Gorguel respectively, which shows the low fertility of these soils. Finally, the residues from both ponds are saline with EC values of 3.6 and 4.8 dS/m for Lirio and Gorguel, respectively.

**Table 1. Physico-chemical characteristics of Lirio tailing pond. (unit indicated in the text).**

| Lirio | pH | E.C. | T.N. | O.C. | C.E.C. | Sand | Silt | Clay |
|---|---|---|---|---|---|---|---|---|
| Mean | 5.39 | 3.63 | 0.01 | 0.37 | 16.38 | 60.17 | 32.47 | 7.35 |
| Error | 0.38 | 0.40 | 0.00 | 0.05 | 2.76 | 7.55 | 6.32 | 1.99 |
| Variance | 1.78 | 1.92 | 0.00 | 0.03 | 91.54 | 684.2 | 479.5 | 47.48 |
| Minimum | 3.71 | 2.53 | 0.00 | 0.13 | 0.25 | 3.00 | 8.55 | 1.11 |
| Maximum | 7.67 | 7.39 | 0.02 | 0.67 | 34.77 | 87.00 | 70.89 | 26.11 |

Fractionation of bulk samples into various particle sizes revealed different behavior between tailing ponds. In Gorguel pond, the dominant fraction was 425–150 μm (32%) (Figure 2); the amounts of the smallest fraction (<75 μm) ranged from 7% to 29% (mean 20%) while the largest fraction (425– 2000 μm) varied from 1% to 31% (mean 9%). On the other hand, samples from Lirio pond showed a heterogeneous particle size

distribution; the dominant fraction was 425-150 μm (36%); the smallest fraction represents the 23% of the total, while the coarsest (425– 2000 μm) ranged from 3% to 34%, with a mean value of 16%.

**Table 2. Physico-chemical characteristics of Gorguel tailing pond. (unit indicated in the text).**

| Gorguel | pH | E.C. | T.N. | O.C. | C.E.C. | Sand | Silt | Clay |
|---|---|---|---|---|---|---|---|---|
| Mean | 7.41 | 4.80 | 0.02 | 0.42 | 8.39 | 60.37 | 30.08 | 9.55 |
| Error | 0.12 | 0.66 | 0.01 | 0.07 | 1.49 | 5.14 | 4.41 | 1.95 |
| Variance | 0.19 | 5.31 | 0.00 | 0.05 | 26.80 | 317.51 | 233.23 | 45.49 |
| Minimum | 6.54 | 2.67 | 0.00 | 0.15 | 3.73 | 33.66 | 6.15 | 3.16 |
| Maximum | 7.90 | 9.35 | 0.06 | 0.71 | 18.10 | 88.89 | 54.84 | 28.97 |
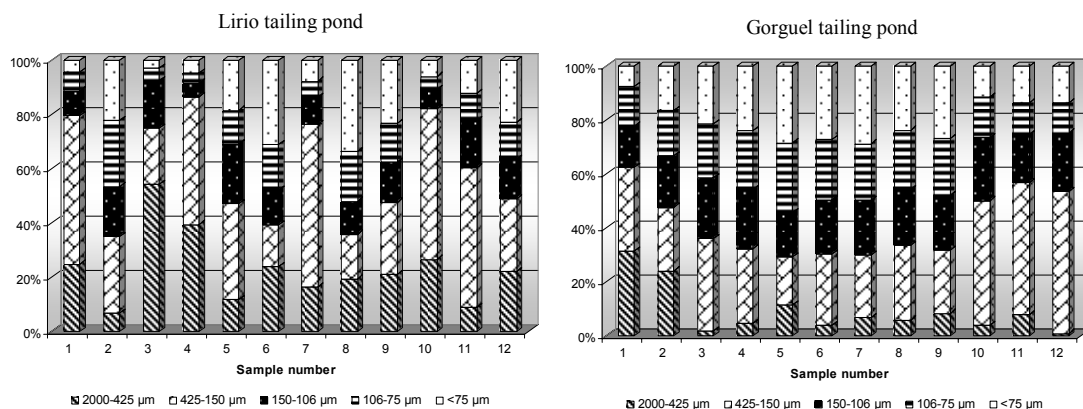


**Figure 2. Contents (%) of five particle size fractions in surface soil from Lirio (left) and Gorguel (right) tailing ponds.**

*Effect of particle size fractions on heavy metal distribution in soil*
Mean concentrations (n=12) of metals in five particle size fractions are shown in Figure 3. As can be seen, high concentration of metals occurred in finest fractions due to a highest surface area and negative charges associated with fine particles. However, in contrast to other studies (e.g. Ljung *et al.* 2006) the coarsest fraction had high concentrations of most of the metals except for zinc and cadmium in Lirio tailing pond. This behavior could be due to the process of treatment of the ore, where biggest particles remain enriched with metals probably because they contain minerals such as galena (PbS) and blende (ZnS). It should be highlighted that the Gorguel tailing pond showed a higher concentration of the metals in most of the fractions and higher increment in the coarsest particles than the Lirio pond, indicating a lower recovery of the metals during the treatment of ore.
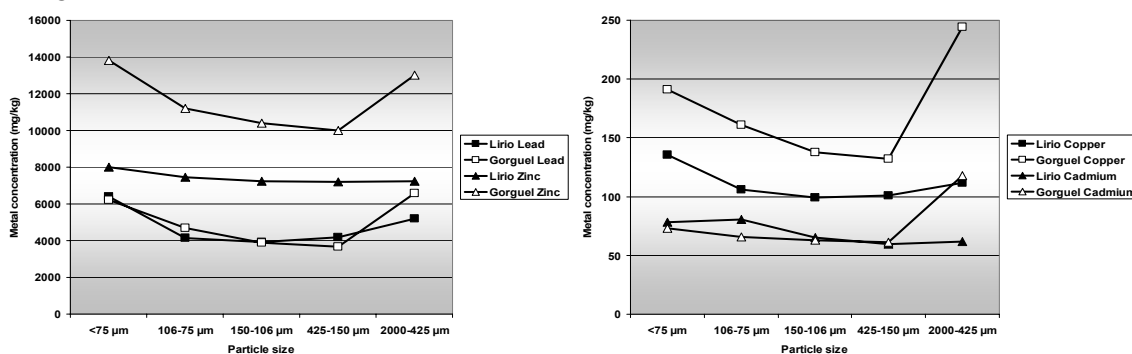


**Figure 3. Mean concentrations of lead (left), zinc (left), copper (right) and cadmium (right) in five particle size fractions for soils from Lirio and Gorguel tailing ponds.**

*Enrichment factor of the metals in particle size fractions*
Figure 4 shows the enrichment factors for Cu, Cd, Pb and Zn in each tailing pond for various particle size fractions. In both ponds, metal enrichment factors (EF) >1.0 were found for Cd, Pb and Zn in all samples, while Cu displays an EF <1 in most of the samples for both ponds. Lirio pond had, for all particle size fractions, EF>10 for Pb; EF>15 for Cd and EF>20 for Zn. On the other hand, Gorguel pond had, for all particle size fractions, EF>10 for Pb; EF>20 for Cd and EF>30 for Zn. These results show the high pollution of these pond soils for all the fractions. The highest EFs were found in finest (<75 μm) and coarsest (2000-425

μm) particles, especially for Zn with EFs>40 for Gorguel tailing pond.
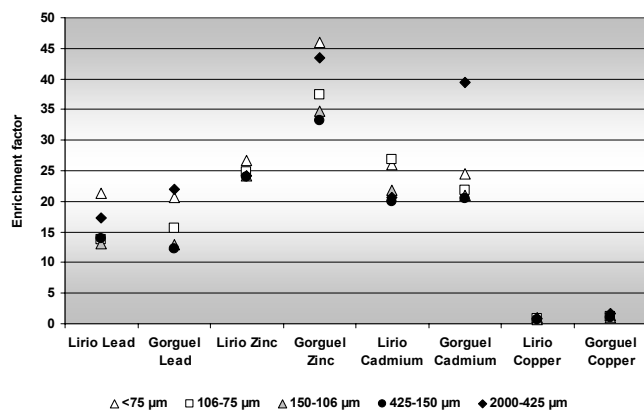


**Figure 4. Mean enrichment factors (EF) of metals in five particle size fractions, in soil surface from Lirio and Gorguel tailing ponds.**

## Conclusion

The characteristics of the studied tailing pond soils prevent plants colonization and leaves their surface unprotected against wind and water erosion, and, as a consequence, pollutants can migrate long distances. This research has showed that high concentration of metals occurred in both finest and coarsest fractions due to high surface area and negative charges associated with fine particles and the processes of ore treatment. The results showed the high pollution of these ponds for all the fractions with enrichment factor (EF)>1. However, highest EFs were for the finest (<75 μm) and coarsest (2000-425 μm) particles with EFs >10 for Pb; >15 for Cd and >20 for Zn in Lirio and EFs>10 for Pb; >20 for Cd and >30 for Zn in Gorguel.

## Acknowledgements

## References

Banat KM, Howari FM, Al-Hamad AA (2005.) Heavy metals in urban soils of central Jordan: Should we worry about their environmental risks? *Environmental Research* **97**, 258–273.

Bower CA, Wilcox LV (1965) Soluble salts. In 'Methods of Soils Analysis part 2'. (ED CA Black) pp. 933-940. (American Society of Agronomy. Madison, Wisconsin, USA)

Chan LS, Davis AM, Yim WWS, Yeung CH (2001) Magnetic properties and heavy metal contents of contaminated seabed sediments of Penny´s bay, Hong Kong. *Mar. Pollut. Bull.* **42**, 569-583.

Chapman HD (1965) Cation Exchange Capacity. In 'Methods of Soils Analysis part 2'. (ED CA Black) pp. 891-900. (American Society of Agronomy. Madison, Wisconsin, USA)

Duchaufour Ph (1970) 'Precis de Pedologie'. (Masson: Paris).

FAO-ISRIC (1990) 'Guidelines for soil description'. 3rd edition. (FAO: Rome).

Lin ZX, Harsbo K, Ahlgren M, Qvarfort U (1998) The source and fate of Pb in contaminated soils at the urban area of Falun in Central Sweden. *Science of the Total Environ*. **209**, 47–58.

Ljung K, Selinus O, Otabbong E, Berglund M (2006) Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry* **21**, 1613–1624.

Madrid L, Diaz-Barrientos E, Madrid F (2002) Distribution of heavy metal contents of urban soils in parks of Seville. *Chemosphere* **49**, 1301–1308.

Peech M (1965): Hidrogen-ion activity. In 'Methods of Soils Analysis part 2'. (ED CA Black) pp. 914-916. (American Society of Agronomy. Madison, Wisconsin, USA)

Risser JA, Baker DE (1990) Testing soils for toxic metals. In 'Soil Testing and plant analysis'. 3rd edition. (Ed RL Westerman) pp. 275-298. (American Society of Agronomy. Madison, Wisconsin, USA).

Wang X, Qin Y, Chen Y (2006) Heavy meals in urban roadside soils, part 1: effect of particle size fractions on heavy metals partitioning. *Environ. Geology* **50**, 1061–1066.

# Immobilization of perfluorooctane sulfonate on modified natural materials: Remediation strategy for contaminated soils

Piw Das[A,B], Venkata Kambala[A,B], Megharaj Mallavarapu[A,B] and Ravi Naidu[A,B]

[A]Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[B]CRC for Contamination Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.

## Abstract

Perfluorinated compounds such as perfluorooctane sulfonate (PFOS) are distributed globally in many wildlife species, as well as ocean waters and even in remote regions far from sources. Limited data available indicate that soil and sediments could act as a major sink for PFOS in the environment. The present work was undertaken to develop a cost effective remediation strategy for the soils impacted with perfluorinated compounds. To this endeavor, a naturally occurring material was modified by our research group and was named as MatCARE[TM] (patent pending). Results obtained show that MatCARE[TM] has a very high sorption capacity for PFOS (50 mg PFOS/g MatCARE[TM]). A treatability study under laboratory conditions was conducted to determine the optimum dosage rate of MatCARE[TM] for the efficient immobilization of PFOS from contaminated soils over a period of 90 days at 25 and 37$^o$C temperatures. The results showed that total immobilization of PFOS occurred at a dosage of 100g/kg of MatCARE in most of the contaminated soils varying in PFOS concentration in the range of 1.83 to 74.38 mg/kg soil.

## Key Words

Perfluorooctane sulfonate, soil, contamination, immobilization, MatCARE[TM].

## Introduction

Perfluorinated compounds (PFCs) manufactured since the 1960s have a wide range of consumer and industrial applications like coatings for textiles, paper packaging products, upholstery, carpeting, insecticides, fabric treatments, paper coatings, corrosion inhibitors, shampoos, anti-static agents, and in the formulations of aqueous fire fighting foams (AFFFs). Perfluorinated surfactants, including perfluorooctane sulfonate, $C_8F_{17}SO_3^-$ (PFOS) have been recently declared as pollutants of environmental concern. The strong carbon-fluorine (C-F) bond of these compounds impart stability to the molecules enabling them to become resistant to thermal, chemical, and biological degradation. Inevitably they have been found to bioaccumualate in higher trophic level organisms through the food chain (Tomy *et al.* 2004). The detection of PFOS in wildlife even in and around the polar regions indicate the long range transport and global distribution of PFOS and its precursors (Moody *et al.* 2003).

AFFFs containing perfluorinated compunds like PFOS have proven to possess very high capacity to fight class B fires or fires from hydrocarbon burning and thus they have been used routinely by civilian and military fire fighters. Historically, effluents from AFFF fire-fighting activities were not pre-treated prior to their discharge in the environment. As a result they have impacted water bodies and soils of a large number of fire training areas including those located in Australia. The important roles of soils and sediments in determining the environmental fate of hydrophobic organic contaminants have long been understood (Luthy *et al.* 1997). Hydrophobic contaminants such as perfluorinated compounds including PFOS are expected to partition from the water column into organic matter rich sediments and soil particles due to their propensity to adsorb to organic carbon thus causing soils to be the ultimate sink for these compounds (Higgins *et al.* 2005, Nakata *et al.* 2006). Application of conventional treatment techniques such as soil washing for remediating perfluorinated compounds from impacted soils is restricted by technical and/or economical constraints. Due to their strong stability, these compounds are also not amenable to biological treatments. Adsorption to suitable and inexpensive adsorbents could be considered a cost effective method for remediating sites contaminated with PFOS and its precursors. The present study was undertaken with the objective of remediating soils collected from fire training areas in Australia where AFFF formulations are used. With this aim, several natural materials were tested to ascertain the one best suited for the purpose of immobilizing PFOS. Subsequently, an attempt was made to optimize the dose at which the material needs to be applied to mitigate the adverse effects of the AFFF compounds.

## Methods

Sorption experiments were conducted with three different naturally modified materials (adsorbents) to determine the one with the highest capacity to adsorb PFOS. The experiments were done by equilibrating each adsorbent with aqueous solutions of PFOS varying in the concentration range of 0 to 500 mg/L for 24 hrs. The solutions were then centrifuged, filtered and subsequently analyzed using HPLC-MS.

PFOS was quantified in the impacted soils using 1:1 ethyl acetate: methanol with 7% orthophosphoric acid as the extracting solvent. Also the physico-chemical properties (pH, organic carbon, anionic constituents) of the soils were assessed following standard procedures. Treatability studies were carried out by the addition of 'MatCARE[TM]', the naturally modified material with the highest sorption capacity at the rate of 100g/kg to the naturally impacted soils and also in some spiked soils. The treated soils were incubated at 60% maximum water holding capacity in two temperature controlled rooms (25 and 37°C) to observe the effect of temperature on the release characteristics of PFOS. The amounts of PFOS that became bioavailable, as determined by desorption, with time were determined after 0, 15, 30, 45 and 90 days.

## Results

*Adsorption study*

Among the different natural materials (MatU, MatV, and MatCARE[TM]) tested MatCARE[TM] (Kambala and Naidu, 2009 Patent Pending) was found to adsorb PFOS at a considerably high level (50 mg/g). Figures 1 and 2 represent the Freundlich and Langmuir isotherms for MatCARE[TM].
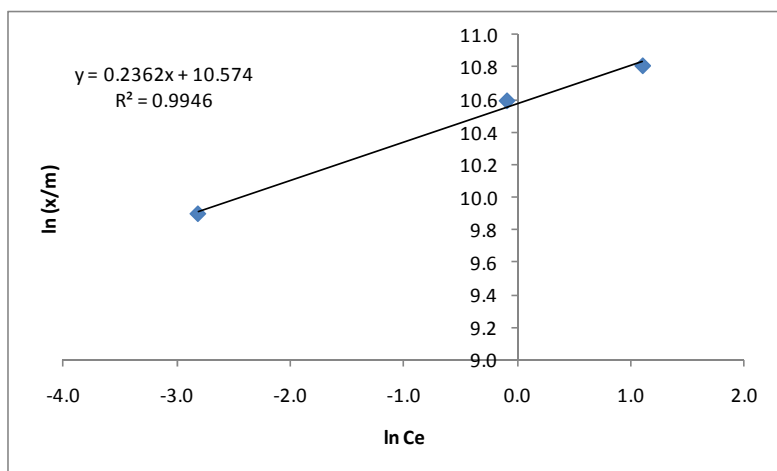


Figure 1. **Freundlich isotherm for MatCARE[TM].**
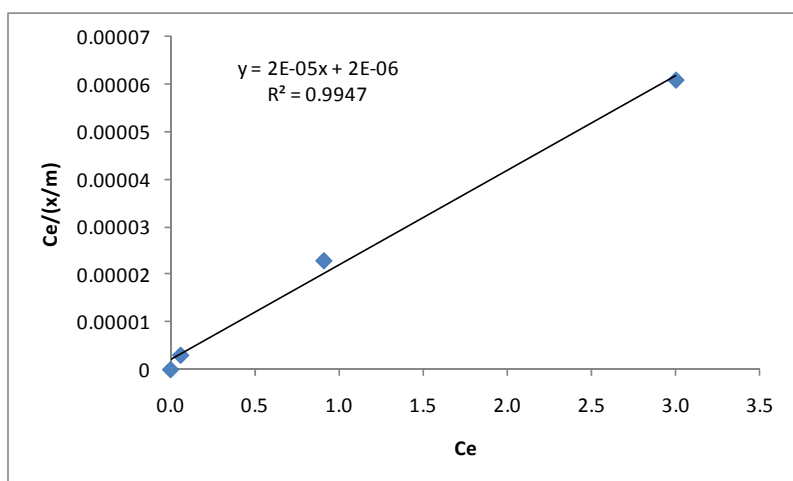


Figure 2. **Langmuir isotherm for MatCARE[TM]**

*Determination of physico-chemical properties of soil*

Four different types of contaminated soils were collected from the impacted sites located in Darwin, Northern Territory, Australia. These soils varied in their physico-chemical properties as can be seen from the data presented in Table 1.

**Table 1. Physico-chemical properties of the soil.**

| Soil | pH | DOC (mg/kg) | TOC (%) | Moisture content (%) |
|---|---|---|---|---|
| Tindal SS01 | 6.46 | 30.57 | 2.03 | 9.64 |
| RBD | 4.37 | 3.07 | 0.96 | 1.94 |
| RBD (Moist) | 5.90 | 32.22 | 1.63 | 24.56 |
| Tindal FTA 064 | 8.10 | 4.55 | 0.29 | 3.02 |

*Treatability studies*

Results from the treatability study performed on the field contaminated soils show that the MatCARE[TM] has a very high capacity to adsorb PFOS and hence to immobilize it. Only in a few cases, insignificant amount of desorption could be found during the entire 90 days incubation period. Figures 3(A) and (B) presents findings of desorption study at 25 and 37°C temperatures. Four soils (RBD, RBD moist, Tindal FTA064, and Tindal SS01) from the impacted areas were amended with MatCARE[TM] at 100 g/kg dosage rate. While the untreated soils showed significant levels of bioavailable PFOS both at 25 and 37°C temperatures as measured by desorption, MatCARE[TM] treated soils showed zero or very low levels of bioavailable PFOS. The RBD soil with a residual concentration of 1.83 mg kg $^{-1}$ PFOS, showed no desorption during the entire 90 day period irrespective of the incubation temperatures (25°C and 37°C). Similar results can be found in case of the Tindal FTA064 soils, which had a PFOS concentration of 16.17 mg/kg. For these soils no release occurred even for the spiked samples with PFOS concentration of 102 and 116 mg/kg, respectively. In case of the RBD moist soil, which had a very high PFOS concentration (74.38 mg/kg), no release could be detected for the naturally contaminated field samples, but for the spiked ones containing 175 mg/kg PFOS, only 3.75 mg/kg PFOS was desorbed at 37°C after 90 day incubation period. The results are similar for the Tindal SS01 soil. While no release could be detected for the naturally contaminated soil with a PFOS concentration of 9.26 mg/kg, only 1.48 mg/kg release was observed in the case of the spiked samples with PFOS concentration of 100 mg/kg. However, no release of PFOS was detected even for the spiked RBD moist and Tindal SS01 soils incubated at 25°C.
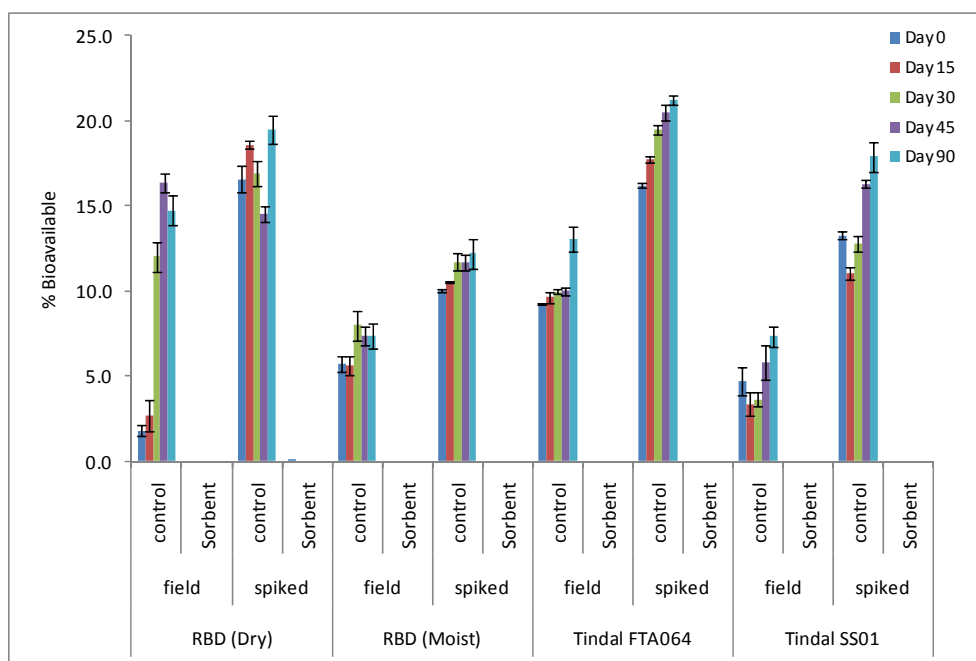


**Figure 3A. Results of desorption study for four different field contaminated and spiked soils at 25°C.**
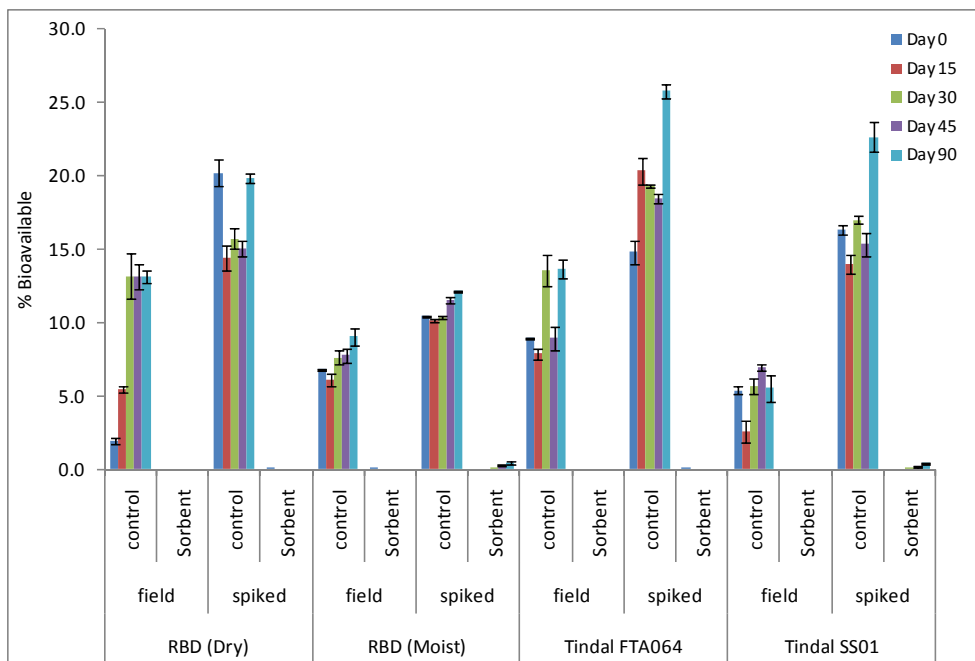
**Figure 3B. Results of desorption study for four different field contaminated and spiked soils at 37°C.**

## Conclusions

It has long been recognized that the transfer of contaminants within the soil profile and their uptake by plants depend to a large extent on the bioavailability of these compounds. Our main strategy to remediate the fire training areas impacted with AFFF compounds was to reduce their bioavailability by adsorption to an inexpensive and nontoxic natural material. 'MatCARE[TM]' developed by CRC CARE/CERAR laboratories was found to be a promising material to immobilize PFOS. Laboratory studies have shown potential outcomes for a field scale remediation trial.

## Acknowledgements

## References

Higgins CP, Field JA, Criddle CS, Luthy RG (2005) Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environmental Science and Technology* **39**, 3946-3956.

Nakata H, Kannan K, Nasu T, Cho HS, Sinclair E, Takemura A (2006) Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat areas of the Ariake sea, Japan: Environmental fate of perfluorooctane sulfonate in aquatic ecosystems. *Environmental Science and Technology* **40**, 4916-4921.

Moody CA, Hebert GN, Strauss SH, Field JA (2003) Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *Journal of Environmental Monitoring* **5**, 341-345.

Tomy GT, Budakowski W, Halldorson T, Helm PA, Stern PA, Friesen K, Pepper K, Tittlemier SA, Fisk AT (2004) Fluorinated organic compounds in an Eastern Arctic marine food web. *Environmental Science and Technology* **38**, 6475-6481.

Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ, Westall JC (1997) Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science and Technology* **31**, 3341-3347.

Kambala V, Naidu R (2009) Tailored natural materials for the remediation of perfluorochemicals in soil and wastewater, Australian Provisional Patent in progress.

# Monitored natural attenuation (MNA) as a cost effective sustainable remediation technology for petroleum hydrocarbon contaminated sites: Demonstration of scientific evidence

Ravi Naidu[A,B], Mallavarapu Megharaj[A,B], Seidu Malik[A,B], Praveen Kumar Rachakonda[A,B], Sreenivasulu Chadalawada[B], Fiona Perso[A,B], Natalie Watkin[A,B], Zuliang Chen[A,B] and Mark Bowman[C]

[A]Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[B]CRC for Contamination Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[C]Department of Defence, Canberra, ACT 2600, Australia.

## Abstract
Recently, monitored natural attenuation (MNA) is recognized as a cost effective and sustainable remediation technology alternative to other engineered technologies for hydrocarbon contaminated sites. However, MNA to be accepted as an appropriate remedy for a contaminated site by the regulators requires demonstration of scientific evidence. This study has evaluated the feasibility of MNA for petroleum hydrocarbons in a long term (>40 years old) contaminated site (soil and groundwater) using a combination of contamination monitoring, biogeochemical indicators, modeling, compound specific stable carbon isotope analysis and molecular microbial techniques. Results demonstrate convincing scientific evidence for natural attenuation of petroleum hydrocarbons by biodegradation rather than dilution or dispersion at this site. Further, this study demonstrates MNA as a defensible remediation technology for petroleum hydrocarbon contaminated sites besides offering suitable methods for evaluation of MNA.

## Key Words
Monitored natural attenuation, MNA, petroleum hydrocarbons, contamination.

## Introduction
The flagship project site is RAAF Base Williamtown situated on a flat coastal plain 30 km north of New Castle. This site was chosen because of its representativeness to the potentially contaminated Defence sites elsewhere in Australia. The aquifer in the RAAF Base is unconfined (Tomago Sandbeds) and the general groundwater flow direction is towards south-east with an average hydraulic conductivity of 10 to 20 m/day. Historically, hydrocarbon contamination at the investigation sites at the RAAF Base Williamtown occurred primarily as a result of their former use as fuel storage facilities. The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) in collaboration with Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia and Department of Defence (DoD) has conducted source characterisation of hydrocarbon contamination and the extent of the groundwater plume at Fuel Farm Area 1 (FFA1) and Fuel Farm Area 2 (FFA2) at RAAF Base Williamtown. This investigation demonstrated that the light non aqueous phase liquid (LNAPL) hydrocarbon contamination source is in the 'smear zone / capillary fringe', mostly concentrated at one metre to three metres depth in both areas, within the likely seasonal variations in the depth to water table. Toxicological analysis using algal and plant bioassays indicated that the TPH in the source zone is bioavailable in both areas. Preliminary calculations of the TPH mass in the soil in FFA1 and FFA2 indicated large amounts, 244376 kg in FFA1 and 342302 kg in FFA2 for the worst case scenario. At these TPH levels, it is likely the source will need active remediation. These investigations were limited to characterization of source and groundwater plume followed by bioavailability testing as required by Risk Based Land Management (RBLM) practice.

## MNA – Scientific evidence
Natural attenuation has been used as an option for remediation of groundwater contaminated with hydrocarbons in USA and Europe. However, there is no consensus in Australia among the regulators with regard to the acceptability of natural attenuation as a remediation method. Nevertheless, natural attenuation is being considered an option for remediation of the groundwater plumes at FFA1 & 2. For this, the scientific basis for natural attenuation processes (provision of scientific evidence that the hydrocarbons are really attenuating) in groundwater needs to be documented and the process characterised to gain acceptance by the

regulatory agencies. Regulatory authorities like EPA Victoria attach a high priority to ensure that natural attenuation can be demonstrated through multiple lines of evidence that degradation of the contaminant is occurring (*e.g.* biodegradation). These lines of evidence include documentation of (a) contaminant loss at field scale, (b) presence of biogeochemical indicators of natural attenuation and (c) presence of contaminant degrading microbes. Simple physical processes involving adsorption, dispersion and dilution tend not to be accepted as 'natural attenuation', unless accompanied by biodegradation. A promising development in recent years is to use the stable isotope composition of individual contaminants to detect and quantify the extent of biodegradation in contaminated aquifers and the use of advanced molecular microbiological techniques to detect the catabolic genes.

Hence, CERAR and CRC CARE conducted further studies to demonstrate natural attenuation as a potential option for remediation of hydrocarbon contaminated groundwater at these sites. This study involved (a) characterisation of hydrogeology of the sites, (b) contaminant delineation in soil and groundwater, (c) determining geochemical indicators of natural attenuation (oxygen, methane, iron, sulphate, nitrate etc.), (d) contaminant modelling and plume stability, (e) molecular microbiological techniques to document the presence of catabolic genes/microbes and (f) compound specific stable isotope fractionation of carbon for BTEX in groundwater.

The major findings of this study are:
- Hydrocarbon degrading genes and bacteria are present in the groundwater and soil.
- Bacteria able to utilise petroleum hydrocarbons as sole source of carbon have been isolated and genes characterised.
- Contaminated soil from source area contained hydrocarbon degrading bacteria but at a very low numbers which is due to lack of nutrients.
- Nutrient amendment enhanced the degradation of TPH in contaminated soils from source area while no significant degradation of TPH was observed in nutrient unamended soils.
- Irrespective of nutrient addition TPH was degraded in contaminated groundwater but at a slightly slower rate compared to nutrient amended. This indicates that natural attenuation of TPH occurring in groundwater.
- BTEX was degraded rapidly in both soil and groundwater with nutrient amendment.
- Compound specific stable isotope analysis (CSIA) of water from FFFA1 shows enrichment of $\partial$13C‰ in m-p xylene and naphthalene at the down gradient wells indicating biodegradation is occurring at FFA1.
- Similarly CSIA of water from FFFA2 shows enrichment of $\partial$13C‰ in toluene, ethyl benzene, m-p xylene and naphthalene at the down gradient wells indicating biodegradation is taking place at FFFA2.
- Also stable isotope fractionation indicated the presence of 2 separate spills of hydrocarbons in FFA2.
- Groundwater monitoring data indicate that plume is stable and not expanding.
- Treatability studies suggest nutrient amendment could be a cost effective remediation option for contaminated soil.
- These studies provide multiple lines of scientific evidence that natural attenuation of hydrocarbons is occurring in both the aquifers from FFA1 and FFA2.

In summary, the results of this investigation demonstrate that MNA is a potential remediation option for hydrocarbon contaminated sites at Williamtown RAAF Base. Further, the 'lines of evidence' used in this investigation can serve as a useful approach for demonstration of 'MNA' at other hydrocarbon contaminated sites in Australia.

# Multi-element background for trace elements and radionuclides in soil from Minas Gerais State, Brazil

**Juscimar Silva**[A], Jaime WV Mello[A], Walter AP Abrahão[A], Maurício PF Fontes[A], Luiz S Junior[A], Vanessa P Ferreira[A], Maria HT Taddei[B] and Olguita F Rocha[C]

[A]Soil Department, Federal University of Viçosa (UFV), Viçosa, MG, Brazil, 36570-000, Email juscimarsolos@yahoo.com.br
[B]Brazilian Nuclear Energy Commission (CNEN), Poços de Caldas, MG, Brazil, 37701-970, Email mhtaddei@cnen.gov.br
[C]Minas Gerais Technological Centre (CETEC), Belo Horizonte, MG, Brazil, 30160-030, Email olguitaferreirarocha@gmail.com

## Abstract

Preliminary results of a multi-element geochemical background study in soils from Minas Gerais state, Brazil, are presented. Natural soils without apparent anthropogenic influence were collected to determine the content of trace elements and radionuclides in order to establish their reference values (RV). From the data analysed so far, the content of B, Ba, Cd, Co, Cr, Cu, Mn, Ni, V, and Zn presented a wide variation mirroring the diversity of parent materials. By calculating the 75 percentile (P-75) of the data distribution we observed that our results were higher than the data reported in the literature. Differences between analytical methods and the great variability of tropical soils seem to be the main restriction when the data are compared. Determining RV for trace element and radionuclides, on a regional scale, considering just descriptive statistical data, such as mean or the upper quarter (P-75) may not be realistic due to the great diversity of tropical soils. Hence correlations between trace element and radionuclides data and some soil variables are warranted to better estimate the RV for such soils.

## Key Words

Toxic elements, Regulations, Contamination, Reference values

## Introduction

The state of Minas Gerais, in Brazil, is a well known mineral province, where, in the past, mining activities preceded modern environmental concern and concepts. Consequently, contaminated lands presenting high trace element contents became one of the main legacies of such activities. Nowadays, the intense industrial growth, the current land-use practices, the predominance of urbanization along with the increasing demand for alternative source of energy have caused an unprecedented environmental pressure on the natural resources. Soils have particularly been at risk and possibly endangering the resilience of the ecosystems. As a general observation, natural anomalies associated with high trace elements and radionuclides contents are rather common and supplant the anthropogenic ones. In addition, natural and anthropogenic processes play a key role on the global geochemistry of those elements in soils, waters and sediments. As a result, characterization of these elements provides an important environmental index, as yet little explored in tropical soils.

The knowledge of natural concentration of trace elements and radionuclides in soils without human influence is necessary for assessing the degree of metal pollution affected by anthropogenic activities and inputs (Rojo *et al.* 2004) and before a soil to be declared contaminated. Although incipient in Brazil, the assessment of reference value (RV) is well established in many countries, i.e. United States, Germany, France and the Netherlands. The later was the foremost to publish the RV for trace elements in soils and nowadays presents a rather consolidated method for risk assessment named C-soil.

Distinct parent materials give rise to differences in the distribution of trace elements and radionuclides in soils. Thus important variations can be expected in their contents even in relatively homogeneous soil classes according to pedogenetic standards. Tropical soils, on the other hand, are subject of intense redistribution processes not only along the soil profile, but also laterally that may modify the original geochemical heritage standard. As a result, experimental studies, considering sampling under a wide range of soil types or parent materials, are warranted to elucidate the pedologic standard for distribution of trace elements and radionuclides. The purpose of this paper is to present preliminary results of a multi-element geochemical background study, in natural soils from Minas Gerais state, as a basis to estimate RV for trace elements and radionuclides at a regional level. It is a result of a cooperative project between Universities at the State of Minas Gerais and its Environmental Agency (FEAM).

## Materials and methods
*Study area*
Located in the southeastern of Brazil, Minas Gerais is the second most populous and fourth largest State in the federation, comprising an area of about 588.384 km$^2$. Because it is placed in the inter-tropical zone, the pedologic mantle is mostly composed by well developed soils, such as Latosols (Ferralsols), Argisols (Acrisols), and Nitosols (Nitisols). Kaolinite in associations with iron (hydr)oxides and gibbsite is the dominant clay mineral in those soils (Fontes and Weed 1991). Cambisols occurs to a lesser extent and usually presents latosolic mineralogy.

*Sampling and determination of RV*
Natural soils without apparent anthropogenic influence were collected to determine the RV of trace metal and radionuclides. A total of 270 single samples were taken from undisturbed representative sites and georeferenced by Global Position System (GPS) in order to cover all the soil types (Figure 1). Each site was sampled on an area of at least 1,000 m$^2$ (mostly ca. 10,000 m$^2$) and was situated at a minimum distance of 100 m away from nearby roads. Samples were collected at 0-20 cm depth by manually driven stainless-steel auger. The material was placed into pre-labelled polyethylene bags, after removing larger stones and roots material. Prior to chemical and physical analyses, the samples were air-dried and passed through a 2-mm stainless-steel sieve to obtain the fine earth fraction (< 2 mm). A portion of 10 cm$^3$ of fine earth was ground in agate mortars to a grain size < 75 μm (200 meshes). Care was taken in sampling, preparation and storage to avoid accidental trace metal contamination. Prior to chemical analysis, the samples were dried at 40 °C for 48 h. Aluminium, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sb, Sr, Ti, V, W, and Zn were determined by ICP-OES and HG-ICPOES (Perkin Elmer, 3300DV). The alpha and beta total activity were determined by gamma spectrometry and the content of Th and U by ultraviolet-visible spectroscopy, following microwave extraction methods according to the standard digestion methods proposed by USEPA. Analytical quality was verified using standard reference materials NIST-SRM 2709, 2710, and 2711 for soil and IAEA 433 for radionuclides. All determination was carried out in triplicates.
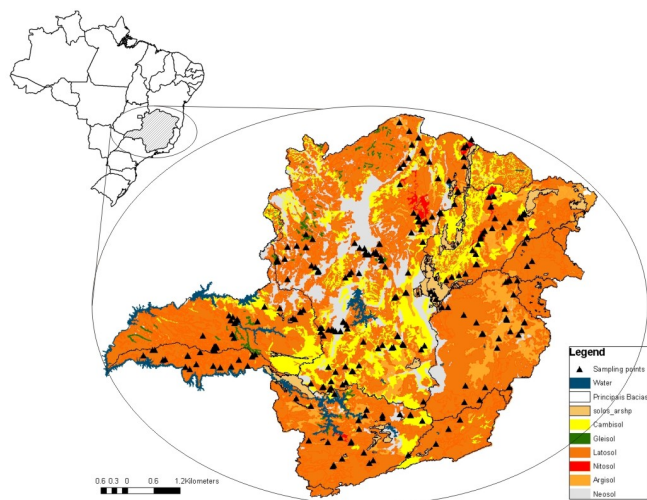


**Figure 1. Sampling sites (black triangles) in Minas Gerais State covering different soil types.**

## Results and discussion
The recovery of elements in standard reference material SRM 2709, 2710, and 2711 were in the range of 80 – 120% of the total certified content. Preliminary results for 190 samples, randomly distributed in the Minas Gerais states, are shown in Table 1. About 80% of the total samples corresponded to soil classes of major occurrence in the state being 104 Latosols, 29 Argisols, and 19 Cambisols. Differences in the parent materials had a remarkable influence in the content of B, Ba, Cd, Co, Cr, Cu, Mn, Ni, V, and Zn where the values presented a wide variation. Except for B the average content of the other elements were lower than those reported by Marques *et al.* (2004) for soils from the Cerrado region in Minas Gerais. Such pattern was already expected as we used the USEPA 3051a leaching method, which does not achieve a complete extraction of the analyte from the sample. A very noticeable B anomaly appears as compared with both, the world soil and Paraná soil averages as reported by Kabata-Pendias and Pendias (2001) and Licht *et al.* (2006), respectively.

**Table 1. Trace elements descriptive statistics in soil samples (n = 190) in comparison with published data.**

| | *B* | *Ba* | *Cd* | *Co* | *Cr* | *Cu* | *Mn* | *Ni* | *V* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|
| | ---------------------------------------------- mg/kg---------------------------------------------- | | | | | | | | | |
| **Min.** | 3.88 | 1.91 | < 0.02[1] | < 0.02 | 1.85 | < 0.02 | 6.99 | < 0.02 | < 0.02 | 2.17 |
| **Max** | 288.06 | 676.77 | 1.62 | 75.37 | 1387.35 | 178.64 | 2212.26 | 505.85 | 570.88 | 234.76 |
| **Mean** | 71.22 | 75.61 | 0.43 | 5.97 | 77.80 | 19.55 | 244.55 | 19.44 | 95.69 | 30.24 |
| **Med** | 55.88 | 51.53 | 0.36 | 1.88 | 49.04 | 12.59 | 136.24 | 12.37 | 58.22 | 23.46 |
| **P-75[2]** | **97.60** | **105.61** | **0.61** | **6.44** | **90.60** | **21.21** | **286.50** | **20.36** | **129.55** | **37.37** |
| **P-90[3]** | **139.37** | **168.88** | **0.91** | **14.94** | **163.44** | **38.01** | **609.90** | **31.65** | **221.31** | **56.42** |
| **WS[4]** | 30 | 500 | | 13 | 65 | 20 | 545 | 20 | 90 | 50 |
| **MG[5]** | | 67 ± 127 | | 5 ± 6 | 112 ± 69 | 33 ± 55 | 455 ± 583 | 14 ± 13 | 257 ± 231 | 38 ± 54 |
| **PR[6]** | 6–99 (24) | 43–502 (147) | | | 43–62 (87) | 20–319 (117) | 135–1980 (538) | | 81–856 (360) | 24–124 (77) |
| **Fadigas *et al.* (2006) P-75** | | | 0.4 | 2 | 43 | 2 | | 12 | | 12 |
| **Lemos (2000) P-75** | | 75 | < 0.5 | 13 | 40 | 35 | | 13 | 275 | 60 |

[1]/Values followed by the < signal mean the detection limit; [2]/Upper quarter (75 percentile of the frequency distribution); [3]/90 Percentile of the frequency distribution; [4]/World Soil (Kabata-Pendias and Pendias 2001); [5]/ Minas Gerais Cerrado soils (mean ± standard deviation; Marques *et al.* 2004). [6]/ Paraná soils (Licht *et al.* 2006; n = 307)

Despite B being highly mobile under oxidizing and acidic conditions, its enrichment can be due to the presence of a large calcareous province in Minas Gerais. It is well known that calcareous soils often show a relatively high B enrichment, inherited mainly from parent rock material. Establishing RV for trace elements in soils is rather subjective and depends on the criteria regionally defined. Two parameters related to data distribution frequency have been used, i.e. 75 percentile (upper quarter P-75) and 90 percentile (P-90). The former is more conservative and has been preferred in environmental agencies which are concerned about the fate of the contaminants in the geoecosystem. In this work, the values corresponding to the P-75 were in general higher than the data reported by Fadigas *et al.* (2006) and Lemos (2000). By considering the similarity of soils classes used by Fadigas *et al.* (2006) such behaviour would not be expected. The results discrepancy could again be attributed to differences between analytical methods since they used aqua regia as extractor. In fact large differences between aqua regia and USEPA 3051a methods are not expected, but Campos *et al.* (2003) obtained Pb contents using the USEPA 3051a, in average, 29% higher than those reported by Pierangeli *et al.* (2001) to similar Brazilian soils, but using aqua regia as extractor. The differences can also be ascribed to the sampling method as the majority (60%) of the samples used by Fadigas *et al.* (2006) were taken from sub-soil layer (> 30 cm). Higher values of P-75 observed for Ba (105.61 mg/kg), Cd (0.61 mg/kg), Cr (90.60 mg/kg), and Ni (20.36 mg/kg) as compared to the data reported by Lemos (2000) to soils from São Paulo State are not expected. Basaltic rocks, which are naturally enriched in those trace elements, are common parent materials for soils in São Paulo. On the other hand, in Minas Gerais State the lithology is quite variable, being common soils derived from granitic rocks.

## Conclusion

Determining RV for trace element and radionuclies by considering just descriptive statistic data, such as mean or upper quarter (P-75) may not be realistic due to the great diversity of tropical soils. Therefore, the correlation between the results and some soil variables is warranted to better estimate the RV.

## Acknowledgment

## References

Fadigas FS, Amaral Sobrinho NM, Mazur A, Anjos LHC (2006) Estimation of reference values for cadmium, cobalt, chromium, nickel, lead, and zinc in Brazilian soil. *Communication in Soil and Plant*

*Analyses* **37**, 945-959.

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants. 3rd ed. CRC Press, Boca Raton, 432 p.

Lemos MMG (2000) Metodologia adotada para o estabelecimento dos valores de referência de qualidade para solos e águas subterrâneas no estado de São Paulo. In 'CETESB. Prevenção e Controle da Poluição do Solo e das águas Subterrâneas', CETESB: São Paulo, pp. 68-77.

Licht OAB, Xuejing X, Qin Z, Miyazawa M, Ferreira FJF, Plawiak RAB (2006) Average reference values of geochemical and geophysical variables in stream sediments and soils, State of Paraná, Brazil. *Boletim Paranaense de Geociências* **58**, 59-87.

Marques JJ, Schulze DG, Curi N, Mertzman SA (2004) Trace element geochemistry in Brazilian cerrado soils. *Geoderma* **121**, 31-43.

Fontes MPF, Weed SB (1991) Iron oxides in selected Brazilian Oxisols: I. Mineralogy. *Soil Science Society of America Journal* **55**, 1143-1149.

Pierangeli MAP, Guilherme LRG, Curi N, Silva MLN, Oliveira LR, Lima JM (2001) Teor total e capacidade máxima de adsorção de chumbo em Latossolos brasileiros. *Revista Brasileira de Ciência do Solo* **25**, 279-288.

Rojo P, Frances F, Garcia-Sanchez A, Alvarez-Ayuso E (2004) Baseline concentrations of heavy metals in native soils of the Salamanca and Valladolid provinces, Spain. *Arid Land Research and Management* **18**, 241-25.

# Nitrate leaching and nitrous oxide emissions related to bacteria and not to archaea in nitrogen rich grassland soils

H.J. Di[A,F], K.C. Cameron[A], J.P. Shen[B], J.Z. He[B], C.S. Winefield[C], M. O'Callaghan[D] and S. Bowatte[E]

[A]Centre for Soil and Environmental Quality, PO Box 84, Lincoln University, Lincoln 7647, Christchurch, New Zealand.
[B]Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China.
[C]Faculty of Agriculture and Life Sciences, PO Box 84, Lincoln University, Lincoln 7647, Christchurch, New Zealand.
[D]AgResearch Ltd, Lincoln Research Centre, Private Bag 4749, Christchurch, New Zealand.
[E]AgResearch Ltd, Grasslands Research Centre, Tennent Drive, Private Bag 11008, Palmerston North 4442, New Zealand.
[F]Corresponding author, Email Hong.Di@lincoln.ac.nz

## Abstract

The oxidation of ammonia ($NH_3$) to nitrate ($NO_3^-$) is a key process in the global nitrogen (N) cycle which has major ecological and environmental implications both in influencing nitrous oxide ($N_2O$) emissions and $NO_3^-$ leaching. We investigated the relationships between nitrification, $NO_3^-$ leaching and $N_2O$ emissions with ammonia oxidizing bacteria (AOB) and archaea (AOA) in nitrogen rich grassland soils. Both AOA and AOB were detected in large numbers in these grassland soils. The AOB abundance grew by 3.2 to 10.4 fold and activity increased by 177 fold in response to the addition of a urine-N substrate, and the AOB growth was significantly inhibited by a nitrification inhibitor, dicyandiamide (DCD). However, neither the AOA abundance, nor activity, increased with the application of an ammonia substrate. DCD decreased $NO_3^-$ leaching by 59% and decreased $N_2O$ emissions by 64% from animal urine-N patches. Significant quantitative relationships were found between the AOB abundance and the nitrification rate, $NO_3^-$-N leaching losses, and $N_2O$ emissions, whereas no such relationships were found with AOA. These findings suggest that nitrification and thus $NO_3^-$ leaching and $N_2O$ emissions are driven by bacteria rather than archaea in these nitrogen rich grassland soils.

## Key Words
Ammonia oxidizing bacteria, ammonia oxidizing archaea, nitrification, nitrification inhibitor, nitrate leaching, nitrous oxide emissions, grazed grassland soil.

## Introduction
Nitrification is a key biogeochemical process of the nitrogen (N) cycle which results in the oxidation of ammonia ($NH_3$) to nitrite ($NO_2^-$) and then to nitrate ($NO_3^-$). This process has major environmental and ecological consequences, because it releases nitrous oxide ($N_2O$) which is a potent greenhouse gas and $NO_3^-$ which can be leached to contaminate groundwater and surface waters. The long-term global warming potential of $N_2O$ is c. 310 times that of carbon dioxide ($CO_2$). Nitrate can contribute to surface water eutrophication and is deemed harmful to human health if present at high concentrations in the drinking water. Until recently, the oxidisation of $NH_3$ to $NO_2^-$, was thought to be carried out mainly by autotrophic ammonia-oxidizing bacteria (AOB). Recently, however, the ammonia monooxygenase (AMO) genes have also been found in the domain Archaea, suggesting a potentially important role for ammonia-oxidizing archaea (AOA) (e.g. Leininger *et al.* 2006; He *et al.* 2007; Prosser and Nicol 2008). However, the role of AOB and AOA in ammonia oxidization is not well understood and the relationships between the populations of AOB and AOA and nitrification rate, $N_2O$ emissions and $NO_3^-$ leaching are unknown.

In intensively grazed grassland, e.g. grazed dairy pastures, the largest N source for both $NO_3^-$ leaching and $N_2O$ emissions is the urine-N excreted by the animal during grazing (Di and Cameron 2002a). The nitrogen loading rate under a dairy cow urine patch can be as high as 1000 kg N/ha (Di and Cameron 2002a). Most of the N excreted in the urine is urea which, upon hydrolysis in the soil, is converted to $NH_4^+$, and is thus available for nitrification. One of the recent advances in the mitigation of $NO_3^-$ leaching and $N_2O$ emissions from grazed pastures is the development of an agricultural spray containing a nitrification inhibitor (NI) to inhibit the conversion of $NH_3$ to $NO_3^-$ (Di and Cameron 2002b). However, it remains unclear what role different ammonia-oxidizers (e.g. AOB and AOA) play in nitrification in the soil and what group of ammonia oxidizers are in fact inhibited by the NIs. The objectives of this research were to: (i) study AOB and AOA populations in a range of intensively grazed grassland soils across New Zealand; (ii) determine their relationships with nitrification rate, $N_2O$ emissions and $NO_3^-$ leaching losses; and (iii) determine the effect of dicyandiamide (DCD) nitrification inhibitor on these populations and processes.

## Materials and methods
*Determination of AOB and AOA populations*
Soil samples (0-0.1 m depth) were taken from six different sites across New Zealand: Northland (NL), Waikato (WK), and Rotorua Lakes (RL) in the North Island, and Canterbury (CT), West Coast (WC) and Southland (SL) in the South Island and were used in an incubation study under controlled temperature (12°C) and moisture (80% soil water holding capacity) (Details of the soil classifications and properties are found in Di *et al.* 2009a; 2009b; 2009c). The experiment consisted of six soils and each soil had the following treatments: A: Control; B: 50 kg urea-N + 1000 kg urine-N per ha; C: 50 kg urea-N + 1000 kg urine-N + 10 kg DCD per ha. Each treatment was replicated four times. Treatment B was designed to simulate a situation under a dairy cow urine patch in a grazed pasture where the N input from the urine was equivalent to 1000 kg N/ha, and 50 kg of fertilizer N was also applied to the grazed field, including urine patch areas. DCD (dicyandiamide) is a nitrification inhibitor used here to determine its effect on AOB and AOA populations and on nitrification rate. Soil samples were taken at different intervals after the application of the treatments for the determination of the *amoA* gene copy numbers of the AOB and AOA populations. Sub-samples were also extracted with 2 $M$ KCl to determine $NO_3^-$ concentrations and thus give a measure of nitrification rate.

*Determination of nitrate leaching and nitrous oxide emissions*
Large undisturbed soil monolith lysimeters (0.5 m diameter and 0.7 m deep) were collected and used to determine $NO_3^-$ leaching and $N_2O$ emissions (Di *et al.* 2009b; 2009c). The lysimeters were installed at a field lysimeter facility at Lincoln University which is about 20 km south of Christchurch on the east coast of the South Island. The lysimeters were exposed to the same climatic conditions as the soil and pasture in the surrounding field. Two rainfall conditions (1260 mm and 2145 mm p.a.) were created using a rainfall simulation system in order to test the influence of rainfall inputs on $NO_3^-$ leaching and $N_2O$ emissions. Pasture was harvested at typical grazing heights and removed before the application of the treatments and was subsequently cut at typical grazing intervals thereafter. Leachates from the lysimeters were collected as required and analysed for $NO_3^-$, nitrite ($NO_2^-$), and $NH_4^+$ concentrations. A standard closed chamber method was used to determine $N_2O$ emissions from the treated lysimeters (Di *et al.* 2009c).

## Results
*Abundance of AOA and AOB and nitrification rate*
Both AOA and AOB *amoA* genes were detected in large numbers but they varied widely in the six different soils (Di *et al.* 2009a). Phylogenetic analysis showed that all the AOB clones recovered were closely related to the *Nitrosospira* species and no clones were closely aligned with the *Nitrosomonas* species. A majority of the AOA clones identified were closely aligned with the soil clade. Interestingly, a number of the clones were affiliated with cluster Marine, suggesting similarity with AOA of marine origin.

Whilst the AOB populations in the Controls (no nitrogen substrate or NI) of the six soils remained relatively stable over the three month incubation period, they increased by 3.2, 5.7, 9.4, 10.4, 4.7 and 5.4 fold following the application of the urine-N substrate in the NL, WK, RL, CT, WC and SL soils, respectively (Figure 1a). When the nitrification inhibitor, DCD, was applied, the AOB population growth was significantly inhibited (Figure 1a). In contrast, the AOA population abundance remained largely unchanged in all the soils irrespective of the urine-N and inhibitor treatments (Figure 1b). Therefore, in all the soils the AOA populations did not grow with the supply of the large dose of urine-N substrate.

Following the application of the urine-N to the WK soil, the AOB RNA copy numbers increased by more than 177 times, from $1.1 \times 10^2$ in the Control soil to $2.4 \times 10^4$ in the urine-N treated soil (Di *et al.* 2009a). When DCD was applied, the AOB activity was significantly inhibited, with the RNA copy numbers remaining the same as that in the Control. In contrast, the AOA activity did not change with the urine-N application, with the RNA copy numbers remaining the same in the Control, Urine and Urine + DCD treatments. In the Urine treatment, the AOA RNA copy number was only 2% that of the AOB.

In all six soils, the addition of the urine-N substrate significantly increased the nitrification rate, as indicated by the rising $NO_3^-$-concentrations, but the nitrification rates were reduced by the NI treatments (Figure 1c).
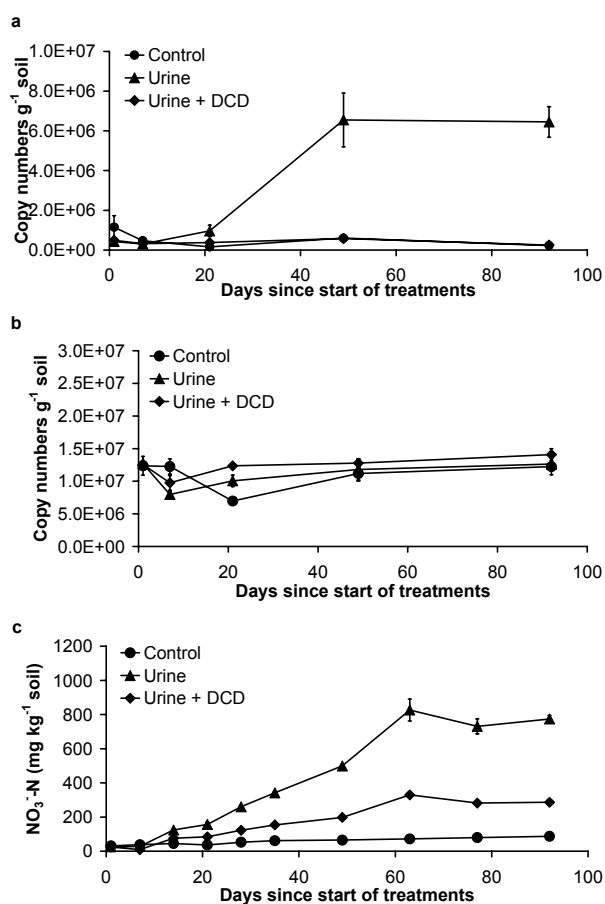
**Figure 1. (a): AOB population abundance; (b): AOA population abundance; and (c): Nitrate-N concentration in the soil, in the Waikato Horotiu soil. Similar trends were found in the other soils.**
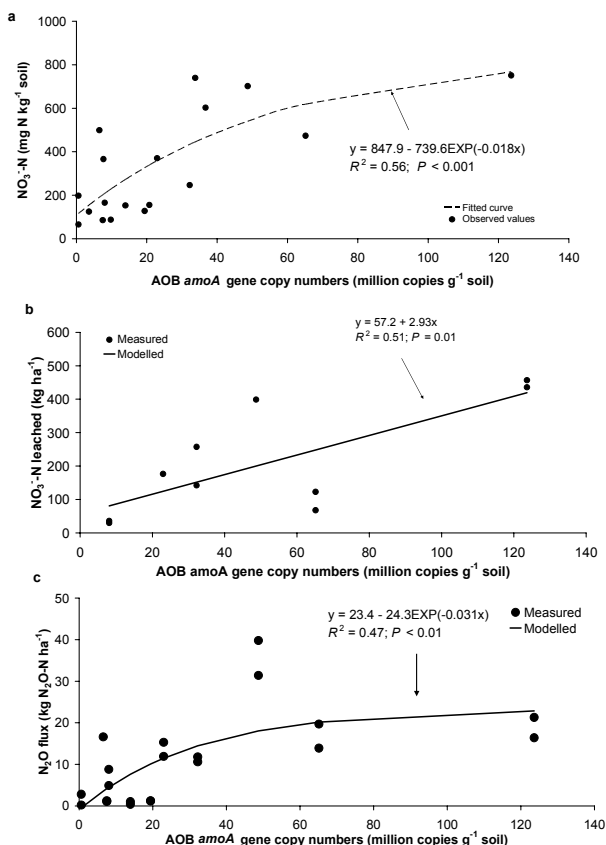
**Figure 2. Relationships between AOB abundance and (a) Nitrification rate; (b) Nitrate-N leaching losses; and (c) Nitrous oxide emissions.**

*Nitrate leaching and nitrous oxide emissions*

Under the 1260 mm rainfall treatment, total $NO_3^-$-N leaching losses in the Urine treatment ranged from a low of 122.9 kg $NO_3^-$-N/ha in the WC Harihari soil to a high of 435.8 kg $NO_3^-$-N/ha in the SL Mataura soil. These were significantly decreased to between 35.8 and 176.5 kg $NO_3^-$-N/ha when DCD was applied ($P < 0.05$). The application of DCD therefore reduced the $NO_3^-$ leaching losses by between 56 to 71%. Under the 2145 mm rainfall condition, the total $NO_3^-$-N leaching losses in the Urine treatment varied from 67.7 kg $NO_3^-$-N/ha in the WC Harihari soil to 457.0 kg $NO_3^-$-N/ha in the SL Mataura soil. These losses were decreased to 29.7 and 257.4 kg $NO_3^-$-N/ha with the application of DCD. The application of DCD therefore reduced these $NO_3^-$ leaching losses by between 44 to 56%. The difference in the amount of $NO_3^-$-N leached between the two rainfall conditions was not statistically significant ($P > 0.05$). The average reduction in $NO_3^-$-N leaching loss by the DCD treatment under both rainfall conditions was 59%.

Total $N_2O$ emissions varied significantly between the different soils, with those in the urine treatment ranging from a low of 13.9 kg $N_2O$-N/ha in the WC Harihari soil under the higher rainfall condition to a high of 39.8 kg $N_2O$-N/ha in the CT Lismore soil under the higher rainfall condition. The different water inputs did not result in significantly different total $N_2O$ emissions ($P > 0.05$). However the DCD treatment decreased the total $N_2O$ emissions from all of the four soils. The emission factor from the urine ($EF_3$) varied from 1.4% to 3.0% (averaging 2.2%), and this was decreased to between 0.3% and 1.4% (averaging 0.8%) with the DCD treatment. Therefore, the DCD treatment resulted in a reduction of the average $EF_3$ by 64%.

*Relationships between ammonia oxidizers and nitrogen losses*

Regression analysis showed a significant exponential relationship between the $NO_3^-$-N concentration and the abundance of the AOB population (Di *et al.* 2009a) (Figure 2a). Therefore, as the AOB population abundance increased the nitrification rate increased exponentially. However, no quantitative relationship was found between the $NO_3^-$-N concentration and the abundance of AOA populations. A significant relationship

was found between total $NO_3^-$-N leaching loss from both rainfall treatments of the soils and the AOB *amoA* gene copy numbers (Di *et al.* 2009b) (Figure 2b), but no relationship was found with the AOA populations. A significant exponential relationship was also found between the total $N_2O$ emissions and the AOB populations after 49 days of incubation (when the AOB population peaked in most of the urine treatments) (Di *et al.* 2009c) (Figure 2c) but no quantitative relationship was found with AOA populations.

**Conclusions**
AOB and AOA populations were present in large numbers in the New Zealand grassland soils. However, in the nitrogen rich urine patch soils, only the AOB population grew and activity increased when supplied with the high dose of ammonia substrate in the urine. The AOB population and activity were also significantly inhibited by the nitrification inhibitor DCD. The AOA population abundance and activity did not grow when supplied with the high dose of ammonia substrate (urine). The nitrification inhibitor DCD significantly decreased nitrate leaching by an average of 59% under two contrasting rainfall conditions (1260 mm and 2145 mm p.a.), and significantly decreased nitrous oxide emissions by an average of 64%. Significant quantitative relationships were found between the nitrification rate, nitrate leaching losses and nitrous oxide emissions with AOB abundance, but not with the AOA abundance. These results suggest that nitrification, and thus nitrate leaching and nitrous oxide emissions, are driven by AOB rather than AOA in these nitrogen rich grassland soils with animal urine-N inputs.

**References**
Di HJ, Cameron KC (2002a) Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems* **64**, 237-256.

Di HJ, Cameron KC (2002b) The use of a nitrification inhibitor, dicyandiamide (DCD), to reduce nitrate leaching from cow urine patches in a grazed dairy pasture under irrigation. *Soil Use and Management* **18**, 395-403.

Di HJ, Cameron KC, Shen JP, Winefield CS, O'Callaghan M, Bowatte S., He J.Z. (2009a) Nitrification driven by bacteria and not archaea in nitrogen rich grassland soils. *Nature Geoscience*. **2**, 621-624.

Di HJ, Cameron KC, Shen JP, He JZ, Winefield CS (2009b) Nitrate leaching from grazed grassland as affected by a nitrification inhibitor, dicyandiamide, and relationships with ammonia oxidizing bacteria and archaea. *Soil Use and Management* **25**, 454-461.

Di HJ, Cameron KC, Sherlock RR, Shen JP, He JZ, Winefield CS (2009c) Nitrous oxide emissions related to bacteria and not to archaea in nitrogen rich grassland soils. *Journal of Soils and Sediments* DOI 10.1007/s11368-009-0174-x.

He JZ, Shen JP, Zhang LM, Zhu, YG, Zheng YM, Xu MG, Di HJ (2007) Quantitative analyses of the abundance and composition of ammonia-oxidizing bacteria and ammonia-oxidizing archaea of a Chinese upland red soil under long-term fertilization practices. *Environmental Microbiology* **9**, 2364-2374.

Leininger S, Urich T, Schloter M, Schwark L, Qi J, Nicol GW, Prosser JI, Schuster SC, Schleper C (2006) Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature* **442**, 806-809.

Prosser JI, Nicol GW (2008) Relative contributions of archaea and bacteria to aerobic ammonia oxidation in the environment. *Environmental Microbiology* **10**, 2931-2941.

# Partitioning of manufactured Ag and CeO$_2$ nanoparticles in relation to soil properties

Geert Cornelis[A], Madeleine Thomas[B], Brooke Ryan[C], Jason K. Kirby[D], Douglas Beak[E], David Chittleborough[F] and Mike J. McLaughlin[G]

[A]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email geert.cornelis@adelaide@edu.au
[B]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email madeleine.Thomas@adelaide@edu.au
[C]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email brooke.ryan@adelaide@edu.au
[D]CSIRO Land & Water, Urrbrae, SA, Australia, Email jason.kirby@csiro.au
[E]CSIRO Land & Water, Urrbrae, SA, Australia, Email doug.beak@csiro.au
[F]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email david.chittleborough@csiro.au
[G]CSIRO Land & Water, Urrbrae, SA, Australia, Email mike.mclaughlin@csiro.au

## Abstract

Soils are likely to be increasingly exposed to manufactured nanoparticles (MNP), but a better understanding of the influence of soil properties on their fate can improve risk assessment. The solid-liquid partitioning ($K_d$) and dissolution of silver (Ag) MNP and cerium oxide (CeO$_2$) MNP was determined after spiking soils of varying properties and compared with soluble Ag(I), Ce(III), and Ce(IV) and bulk Ag(0) and bulk CeO$_2$(s). In addition, MNP $K_d$ values were determined in the same soils made sodic, after the addition of biosolids, or with increased chloride and phosphate concentrations. $K_d$ values for MNP were mostly not significantly different than for soluble analogues but were much lower than for bulk powders. High clay content was suggested to increase $K_d$ MNP, and especially in the presence of high Cl concentrations, 39% of added Ag MNP was dissolved. The presence of phosphate in soil suspensions decreased the $K_d$ values in clayey soils from values higher than 10000 to values lower than 30 for CeO$_2$ MNP that appeared to dissolve much less than Ag MNP. The fate of Ag MNP and CeO$_2$ MNP in soils thus appears to be determined by more factors than have to date been investigated.

## Key Words

Nanoparticles, partitioning, soil, silver, cerium.

## Introduction

Ag MNP and CeO$_2$ MNP are amongst the most widely used MNP today (Maynard and Michelson, 2007), making use of the optical, mechanical and catalytic properties that are vastly different to more coarsely grained (bulk) powders of the same material (Klaine *et al.* 2008). The same properties can lead to toxic effects when organisms are exposed to Ag MNP and CeO$_2$ MNP (Navarro *et al.* 2008; Van Hoecke *et al.* 2009), but the high surface reactivity possibly result in a strong adhesion to reactive surfaces of soil solids, which potentially reduces exposure of terrestrial organisms to NP in pore water, the major exposure pathway for contaminants in terrestrial systems (e.g. Tong *et al.* 2007). The solid/liquid partitioning of Ag MNP and CeO$_2$ MNP is therefore of primary importance to efficiently assess their risk in soils, but has to date scarcely been investigated. Element partitioning is usually expressed as a $K_d$ value that is calculated as $K_d=M_{solid}/[M]$ [L/kg] where $M_{solid}$ is the geogenic or spiked element concentration expressed on a soil-weight basis (mg/kg) and $[M]$ is the aqueous element concentration expressed on a solution volume basis (mg/L). High and low values indicate strong sorption or preferential partitioning to the soil porewater respectively. $K_d$ values are usually related to soil properties for risk assessment (Sauve *et al.* 2000), but such relations have not yet been established in the case of Ag MNP and CeO$_2$ MNP. In this study, the effect of biosolid addition, sodicity and ions that form precipitates with soluble Ag or Ce forms on solid-liquid partitioning ($K_d$) of Ag MNP and CeO$_2$ MNP was investigated and NP partitioning was compared with soluble and bulk analogues. Sodicity affects 10% of arable land worldwide (Szabolcs, 1989) and predominance of sodium in porewaters is likely to increase NP dispersion (Klaine *et al.* 2008). Biosolid addition has been defined as the main exposure route of soils to NP, particularly in countries were organic-poor soils are amended with biosolids (Mueller and Nowack, 2008), that retain NP in wastewater plants (Kiser *et al.* 2009). NP interaction with dissolved organic carbon (DOC) is known to increases NP mobility in soils (Johnson *et al.* 2009). Ag(I) or Ce(III) ions are the predominant soluble Ag and Ce species in soil porewaters (Kabata-Pendias 2001) and possible formation of cerargyrite (AgCl(s), log$K_s$ = -9.75) and monazite (CePO$_4$(s), log$K_s$= -26.3) may enhance Ag MNP or CeO$_2$ MNP dissolution, again possibly influencing their fate in soils.

**Methods**

*Soil characterization*

Four soils (0-10 cm depth) were air-dried and sieved over 2 mm. EC, pH, Total C, CEC, citrate-dithionite extractable Fe and Al and DOC and particle size analysis were determined according to standard methods (Rayment and Higginson, 1992). Total elemental Ag and Ce concentrations were determined after digestion of soil samples in aqua regia (US-EPA 3051A) and measurement by inductively coupled plasma-mass spectrometry (ICP-MS).

*Ag MNP and CeO$_2$ MNP partitioning and dissolution*

Partitioning of Ag MNP and CeO$_2$ MNP was determined according to Cornelis (2009). Stable Ag MNP and CeO$_2$ MNP were prepared by suspending 0.01 g/L Ag MNP and CeO$_2$ MNP in ultrapure water and 0.5 mM citrate adjusted to pH 10 with NaOH, respectively. After 3 min sonication, the suspensions were filtered with 0.20 μm filters (Sartorius) to remove large aggregates. Five replicates of 2.5 g of each soil were weighed in 50 mL centrifuge tubes to which 22.5 mL of 2.22 mM KNO$_3$ was added. While sonicating stock Ag MNP or CeO$_2$ MNP stock suspensions, 2.5 mL of suspension was added to all soil equilibrations to obtain final spike concentrations of 1.70 mg Ag/kg and 1.30 mg Ce/kg and leading to a final 2 mM KNO$_3$ concentration. In addition, ten replicates of 2.5 mL stock solutions were digested and analysed for total Ag and Ce to confirm MNP addition rate. The spiked suspensions were equilibrated for 24 h in an end-over-end shaker followed by centrifugation at 2100 g for 15 min. The supernatant was filtered using 0.45 μm microfiltration (MF) filters (Millipore) followed by 2 mL filtered with centrifugal ultrafiltration (UF) devices (Pall-Gellman). All UF filters and MF filters in the case of Ag were Cu-preconditioned according to Cornelis *et al.* (2009) to improve Ag and Ce recovery. Ten mL of the MF filtrates was added to open digest vessels for digestion with 65% HNO$_3$ and Ag or Ce determination with ICP-MS. Ag and Ce were determined in UF filtrates without prior digestion.

*Partitioning of soluble Ag(I), Ce(III), Ce(IV) and bulk Ag(0) and bulk CeO$_2$(s)*

2.5 g of each soil was equilibrated in 25ml of 2 mM KNO$_3$, or AgNO$_3$, Ce(NO$_3$).6H$_2$O or (NH$_4$)$_2$Ce(NO$_3$)$_6$ dissolved in 2 mM KNO$_3$ for geogenic, soluble Ag, Ce(III) or Ce(IV) $K_d$ determination respectively. Similar Ag and Ce spiking rates were applied for soluble as for MNP partitioning. The partitioning of bulk powders in soils was examined by adding 0.1 g of metallic Ag(0) (Fluka) or CeO$_2$(s) (Aldrich) powders to five replicates of 50 g of each soil, equilibrated with 500 mL of 2 mM KNO$_3$ which resulted in addition rates of 2027 mg/kg Ag and 2462 mg/kg CeO$_2$. Partitioning determination was executed as described above.

*Partitioning and biosolid addition*

Biosolids were sampled at Bolivar Wastewater Treatment Plant, South Australia, and dried for 30 min at 60 °C and sieved to < 2 mm (53.5% moisture content). 0.1g (dry weight) was added to 2.5 g of each soil, which is the equivalent to 80 t/ha or approximately 5 years of application (Clapp and Larson 1994). Partitioning determination was executed as described above.

*Effect of precipitation on partitioning*

The same method and NP spiking rate AgMNP as above was used, but the background electrolyte was 100 mM KCl in case of Ag NP and 0.016 mM K$_2$HPO$_4$ in case of CeO$_2$ instead of 2 mM KNO$_3$. The chosen Cl$^-$ and PO$_4^{3-}$ represent the upper limit and an average concentration respectively of concentrations commonly found in soils (McLaughlin *et al.* 1997; Sims and Pierzynski 2005).

*Partitioning in sodic soils*

Sodicity was induced by leaching 80 g of each soil with a solution containing 2.9 mM NaCl and 0.15 mM CaCl$_2$. Leaching was initiated with 40 mL followed by two times 15 mL after 2h time intervals. 24h after the last leaching step, the soils were dried for 24 h at 30 °C. Sodium adsorption ratios (SAR) were determined by shaking 5g dry soil for 1 hour with 25 mL water. After filtration with a Whatman No.. 42 filter, 1 mL of the filtrate was mixed with 1 mL strontium chloride (SrCl$_2$) to induce clay flocculation. Sodium concentration was measured in the supernatant with a Flame photometer and Ca and Mg were measured with Atomic Adsorption Spectroscopy. Partitioning determination of Ag MNP and CeO$_2$ MNP was subsequently executed as described above.

## Results

Table 1 shows varying properties for the soils used in this study, but overall a low carbon content. Clarke Hill and Tully soil were used exclusively for studying Ag MNP and $CeO_2$ MNP respectively. Figure 1 shows measured nanoparticulate (calculated as the difference in the 0.45 μm - 1kDa filtrates) and truly dissolved (<1kDa) Ag and Ce concentrations that were used to calculate the indicated $K_d$ values. Within this limited set of soils, Ag MNP $K_d$ values appear to increase with the clay content and extracted Al and Fe, but not apparently with other soil parameters such as pH. This relation is less clear in the case of $CeO_2$ MNP, but for both NP, $K_d$ is particularly low in the sandy MC soil, which suggests together with a previous report (Fang *et al.* 2009) that MNPs collision with naturally occurring colloids may lead to aggregates larger than 0.45 μm. As the biosolids contained 39.5% clay, some $K_d$ values were higher after biosolid addition, but the observed increase in DOC (data not shown) possibly stabilised NP suspensions (Johnson *et al.* 2009) leading to $K_d$ decreases especially in the soils that were already quite clayey. Chloride induced dissolution of Ag MNP, possibly due to $AgCl_4^{3-}$ complexation, but even though dissolved MNP were not included in $K_d$ calculations (Cornelis *et al.* 2009), $K_d$ values were lowered in the presence of chloride. In the case of $CeO_2$ MNP, phosphate addition decreased $K_d$ values as well, but no dissolution was observed. Surface complexation of phosphate anions on $CeO_2$ MNP, increasing its charge and suspension stability, might explain the particularly low $K_d$ values. Sodicity treatments increased SAR ratios from < 0.3 to 8.4 (MC), 2.7 (Em), 3.7 (CH) and 12.4 (Tu), but even though a sodium predominance has been reported to increase NP transport in porous columns (Saleh *et al.* 2008), the effect on partitioning in this study remains unclear. Figure 2 shows that partitioning of bulk powders added to soil were much higher than nanoparticulate analogues as well as soluble Ag(I), Ce(III) or Ce(IV). Soluble Ag(I) partitioning did not differ significantly from Ag NP partitioning and $CeO_2$ partitioning was only significantly lower in MC soil, which can possibly be attributed to the high clay percentage in both Em, CH and Tu soils, but differences in clay percentage apparently did not result in differences in partitioning between Ag MNP and soluble Ag(I).

**Table1. Soil chemical and physical properties**

| Soils | EC dS/ cm | pH | Total C % | Citrate – dithionite ext Al mg/kg | Fe mg/kg | Particle Size Analysis Clay % | Silt % | Sand % |
|---|---|---|---|---|---|---|---|---|
| Mount Compass (MC) | 0.01 | 5.20 | 0.1 | < 100 | < 100 | 1 | 0 | 99 |
| Emerald Black (Em) | 0.1 | 7.49 | 0.9 | 1410 | 11300 | 59 | 14 | 27 |
| Clarke Hill (CH) | 0.1 | 5.27 | 4.9 | 7850 | 8300 | 28 | 40 | 32 |
| Tully (Tu) | 0.3 | 5.00 | 2.75 | 6320 | 700 | 32 | 11 | 57 |
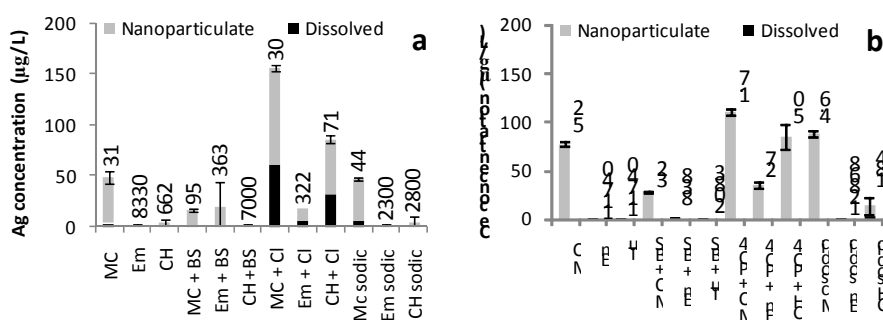


**Figure 1. Measured metal concentrations in <1kDa (dissolved) and <0.45 μm filtrates (dissolved + nanoparticulate) after addition of a) Ag MNP and b) $CeO_2$ MNP to soils in Table 1 with increased sodicity ("sodic"), additional biosolids ("+ BS") or addition of chloride ("+ Cl") or phosphate ("+ $PO_4$"). Error bars are standard deviations (n=4). $K_d$ values calculated from these concentrations are indicated as well.**

## Conclusion

Even though the present study should be extended towards a larger number of soils and treatments, it suggests that Ag MNP and $CeO_2$ MNP are mobile in soils despite their high surface reactivity. Moreover, their fate is determined by more factors than just pH, ionic strength and DOC concentration as suggested by previous reports. Texture was suggested to be a key soil property in determining the fate of these NP and the overall higher solubility of Ag MNP is suggests that these NP will be completely dissolved on the long term, especially in saline (high Cl) soils. In addition, surface complexation of $CeO_2$ MNP can influence partitioning tremendously. To allow an efficient risk assessment of Ag MNP and $CeO_2$ MNP, their partitioning needs to be investigated in a wide range of soils and porewater conditions, with an emphasis on MNP dissolution in conditions.
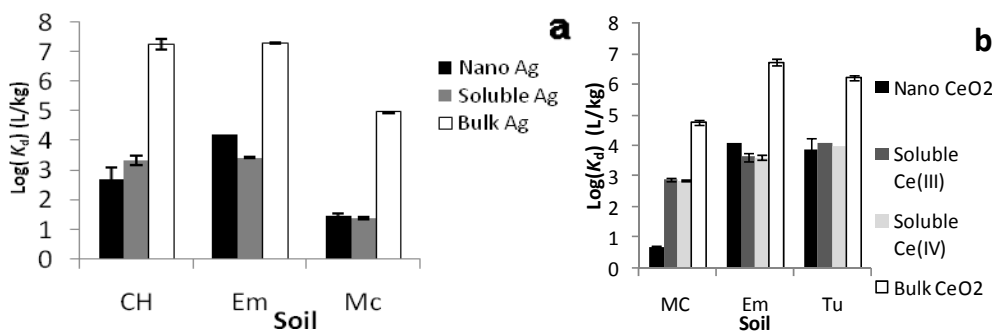
**Figure 2.** Log$K_d$ values of a) Ag MNP compared with soluble Ag(I) and bulk Ag(0) and b) CeO$_2$ MNP compared with soluble Ce(III) and Ce(IV) and bulk CeO$_2$(s). Error bars are standard deviations (n=4).
A partitioning experiment with a 1.30 mg/kg soluble Ce(III) addition in the presence of phosphate resulted in $K_d$ values higher than $10^4$ L/kg in all soils probably due to monazite formation. The $K_d$ decrease of CeO$_2$ MNP upon phosphate addition in Figure 1b can thus not be related to behaviour of soluble Ce(III).

## References

Clapp CE, Larson WE (1994) Sewage Sludge: Land Utilization and the Environment. (Soil Science Society of America: Bloomington).

Cornelis G, Kirby JK, Beak D, Chittleborough D, McLaughlin MJ (2009) A method for determining the partitioning of manufactured silver and cerium oxide nanoparticles in soil environments. *Environmental Pollution* Submitted.

Fang J, Shan XQ, Wen B, Lin JM, Owens G (2009) Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environmental Pollution* **157**, 1101-1109.

Johnson RL, Johnson GOB, Nurmi JT, Tratnyek PG (2009) Natural Organic Matter Enhanced Mobility of Nano Zerovalent Iron. *Environmental Science & Technology* **43**, 5455-5460.

Kabata-Pendias A (2001) Trace elements in soils and plants. Third edition. (CRC press: Boca Raton).

Kiser MA, Westerhoff P, Benn T, Wang Y, Perez-Rivera J, Hristovski K (2009). Titanium Nanomaterial Removal and Release from Wastewater Treatment Plants. *Environmental Science & Technology* **43**, 6757-6763.

Klaine SJ, Alvarez PJJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR (2008) Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environmental Toxicology and Chemistry* **27**, 1825-1851.

Maynard AD, Michelson E (2007) The Nanotechnology Consumer Products Inventory, (PEN: Washington DC)

McLaughlin MJ, Tiller KG, Smart MK (1997) Speciation of cadmium in soil solutions of saline/sodic soils and relationship with cadmium concentrations in potato tubers (Solanum tuberosum L). *Australian Journal of Soil Research* **35**, 183-198.

Mueller NC, Nowack B (2008) Exposure modeling of engineered nanoparticles in the environment. *Environmental Science & Technology* **42**, 4447-4453.

Navarro E, Piccapietra F, Wagner B, Marconi F, Kaegi R, Odzak N, Sigg L, Behra R (2008) Toxicity of Silver Nanoparticles to Chlamydomonas reinhardtii. *Environmental Science & Technology* **42**, 8959-8964.

Rayment GE, Higginson FR (1992) Australian laboratory handbook of soil and water chemical methods. (Inkata Press: Melbourne).

Saleh N, Kim HJ, Phenrat T, Matyjaszewski K, Tilton RD, Lowry GV (2008). Ionic strength and composition affect the mobility of surface-modified Fe-0 nanoparticles in water-saturated sand columns. *Environmental Science & Technology* **42**, 3349-3355.

Sauve S, Hendershot W, Allen HE (2000) Solid-Solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter. *Environmental Science & Technology* **34**, 1125-1131.

Sims JT, Pierzynski GM (2005. Chemistry of Phosphorus in Soils, in, Chemical Processes in Soilsed. (Eds.)MA Tabatabai, DL Sparks) (Soil Science Society of America: Washington).

Szabolcs I (1989). Salt affected soils. (CRC Press: Boca Raton).

Tong Z, Bischoff M, Nies L, Applegate B, Turco RF (2007) Impact of Fullerene (C60) on a Soil Microbial Community. *Environmental Science & Technology* **41**, 2985-2991.

Van Hoecke K, Quik JTK, Mankiewicz-Boczek J, Schamphelaere KACD, Elsaesser A, Meeren PVd, Barnes C, McKerr G, Howard CV, Meent DVD, RydzynÌ ski K, Dawson KA, Salvati A, Lesniak A, Lynch I, Silversmit G, Samber BrD, Vincze L, Janssen CR (2009) Fate and Effects of CeO2 Nanoparticles in Aquatic Ecotoxicity Tests. *Environmental Science & Technology* **43**, 4537-4546.

# Pig slurry as organic fertiliser: a cooperative project

Melisa Gómez[A], Maria Dolores Estevez[A], Angel Faz[A], Ana Belén Olivares[B] and Vicente Climent[A]

[A]Agrarian Science and Technology Department.  Technical University of Cartagena, Murcia, Spain, Email melisa.gomez@upct.es
mariadolores.estevez@upct.es; angel.fazcano@upct.es; Vicente.Climent@upct.es.
[B]Agricultural Cooperative Federation of Murcia (FECOAM), Murcia, Spain, Email aolivares@fecoam.es

## Abstract

In Murcia, SE Spain, the number of intensive pig farms has increased in the last 20-25 years. They are concentrated in a small area, and slurry management has become an important problem for the farmers. The agronomical use of these organic wastes contributes to the reduction of gas emissions, the restoration and reclamation of agricultural and marginal lands, improve the amount and quality of stable organic matter and fights against progressive desertification processes. For this reason, a project has been created where farmers can use the manure stored in pig farms as an organic fertiliser. In this way, slurry and soils samples have been analysed to understand their physical and chemical characteristics before and after use as a soil amendment. Then, pH, electrical conductivity (CE), N content, P content and organic C, were studied in order to determine the application dose for agricultural soils.

## Key Words

Manure management, agricultural use, slurry pig, organic fertiliser.

## Introduction

Intensive and industrial systems have enormously increased the numbers of animals farmed globally and will continue to do so. On intensive pig farms, the animals are generally kept on concrete with slats or grates for the manure to drain through. The manure is usually stored in slurry form (a liquid mixture of urine and faeces). One possible solution for this problem is to incorporate manure immediately into the soil following field application. But in some regions the soils, because of coarse texture or drainage characteristics, are not suitable for utilizing hog manure effectively as a nutrient resource, and this problem results in a risk of pollution of water by nitrogen and phosphorus. Therefore there is a need to develop manure application guidelines so that manure nutrients are applied at rates not exceeding the capability of specific crops to utilize these nutrients. The availability of plant nutrients from manure depends on its composition and on other factors such as management practices and soil characteristics. Thus, the main objective of this work was to find out a practical solution for waste manure management for pig farmers in order to find an economical solution for organic fertilization and avoid the nitrogen and phosphorus pollution of land and water.

## Methods

This work was carried out in the region representing the first area in Murcia, SE Spain, with the highest pig production, as well as is the most important horticultural area. In this way we established a system that put in contact pig farmers with farmers to collect the slurry storage for their evaluation and land distribution. The soil and pig slurry samples were collected in two consecutive years, 2008 and 2009.Soil samples were collected at surface level and at a depth of 30cm, with and without slurry application in order to see the influence of this application in soil composition. All the samples were analyzed by standards methods to obtain the texture classification for determining soil suitability for manure application, values of total N (Duchafour 1970), pH (Peech 1965), electrical conductivity (Bower and Wilcox 1965) and total P (Watanabe and Olsen 1965).

## Results

Table 1 to 4 show the values of pH, electrical conductivity (EC) and total nitrogen, as well as the total phosphorous (Watanabe and Olsen, 1965) in soil and each slurry pond studied. The N maximum dose of application is mandatory regulated (RD 324/2000) and established as 170 kg /ha/year in special sensitive areas. In this work the dose of slurry to apply has been calculated based on N content.

The pH values ranged from 7.6 to 8.3 corresponding with a basic soil (Porta *et al.* 1999). The electrical conductivity ranged between 1.5 and 0.2 dS/m at 25ºC with similar values from surface to 30 centimetres depth. Changes in the chemical composition of the soil caused by application of manure are much influenced by factors such as soil texture, rate, time and method of application of manure, the amount of local precipitation,

**Table 1. pH and EC (dS/cm) soil data values obtained for samples collected in 2008.**

| Farmer | F1 | | F2 | | F3 | | F4 | |
|---|---|---|---|---|---|---|---|---|
| | Top | Depth of 30cm | Top | Depth of 30cm | Top | Depth of 30cm | Top | Depth of 30cm |
| pH | 7.83 | 8.19 | 7.81 | 7.86 | 8.35 | 8.09 | 7.64 | 7.8 |
| EC (dS/m) | 0.94 | 0.46 | 1.20 | 1.54 | 0.20 | 0.68 | 0.88 | 1.11 |

**Table 2. Slurry data obtained for samples collected in 2008.**

| Pig farmer | pH | EC (dS/m) | NA (g/L) | NT (g/L) | P (mg/L) |
|---|---|---|---|---|---|
| PF1 | 6.36±0.03 | 30.27±0.21 | 2.12±0.09 | 2.46±0.54 | 94.00±28.8 |
| PF2 | 8.49±0.07 | 44.83±0.74 | 5.22±0.12 | 7.14±0.20 | 134.7±4.0 |
| PF3 | 8.19±0.15 | 25.73±0.32 | 3.00±0.04 | 3.95±0.14 | 177.5±25.5 |
| PF4 | 7.91±0.06 | 33.80±0.42 | 3.31±0.42 | 5.05±0.17 | 207.00±33.0 |

**Table 3. pH and EC (dS/cm) soil data obtained for samples collected in 2009.**

| Farmer | F1 | | F2 | | F3 | | F4 | |
|---|---|---|---|---|---|---|---|---|
| | Sup | Depth of 30cm | Sup | Depth of 30cm | Sup | Depth of 30cm | Sup | Depth of 30cm |
| pH | 7.83 | 8.19 | 7.81 | 7.86 | 8.35 | 8.09 | 7.64 | 7.8 |
| EC (dS/m) | 0.94 | 0.46 | 1.20 | 1.54 | 0.20 | 0.68 | 0.88 | 1.11 |

**Table 4. Slurry data obtained for samples collected in 2009.**

| Pig farmer | pH | EC (dS/m) | NA (g/L) | NT (g/L) | P (mg/L) |
|---|---|---|---|---|---|
| PF1 | 7.12±0.06 | 27.75±0.919 | 2.15±0.63 | 2.51±0.68 | 100.2±0.10 |
| PF2 | 7.79±0.01 | 55.10±0.1 | 6.33±0.01 | 4.58±0.25 | 290.7±0.29 |
| PF3 | 6.95±0.04 | 36.50±0.1 | 2.79±0.07 | 3.12±0.05 | 397.0±0.39 |
| PF4 | 7.44±0.04 | 26.53±1.6 | 2.48±0.02 | 2.93±0.02 | 110.7±0.11 |

and the crops grown, as well as the animal and farm management. With respect to total N content the data showed that the highest concentration of N is also located in the surface for both studied years, even when samples from application area and non application were compared (2.172-0.875 g /kg in 2008, and 1.528-1.025 g/kg in 2009). The levels of total N have no statistical differences before and after slurry application. In both cases the N concentrations were lower than 0.5 % that is the maximum level for agricultural soils (Andrades 1996). Heavy application of manure has been shown to increase $NO_3$-N and available P more rapidly than inorganic fertilizers. Manure application also results in accumulation of $NO_3$-N, and extractable P in the subsoil (Pries 1996). The level of accumulation increased with the rate of application, but in this study the dose applied is low according with the law.

Hog manures have a lower N/P ratio than crop plants. Thus when N is supplied through manure to a crop, more P is applied than is required by the plants and this may result in leaching and runoff of P. If Figure 1 and 2 are compared, it is possible to show the increase of P content after slurry application. This is because the traditional application rates are based on N needs for the crops. This has led often to an increase in soil P level in excess of crop requirements because of the greater N-to-P ratio (average ratio of 4:1).

The texture analysis (Table 5) showed that the predominant textural classes of analyzed soils were clay, clay loam and silt-loam, except for F3 where sand is the predominant textural class (coarse-textured). These results
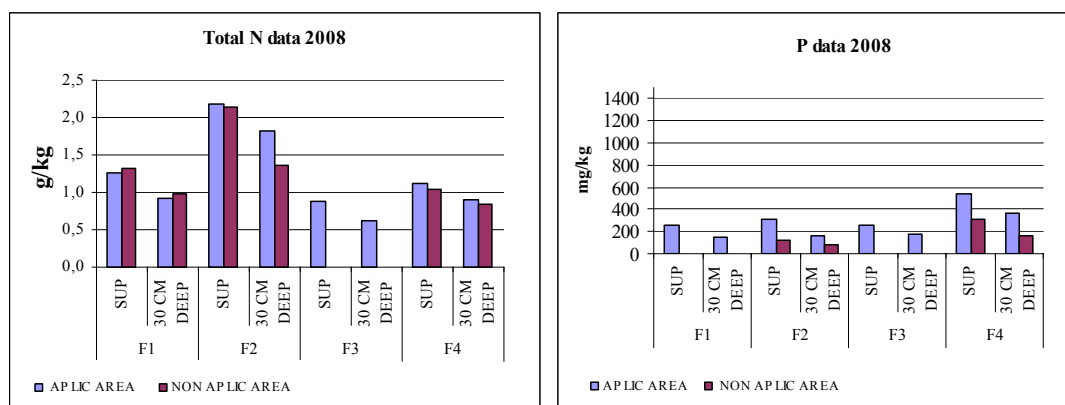


**Figure 1. Graphic representation of total N and soil and $P_2O_5$ soil data values in mg/kg, obtained for samples collected in 2009**
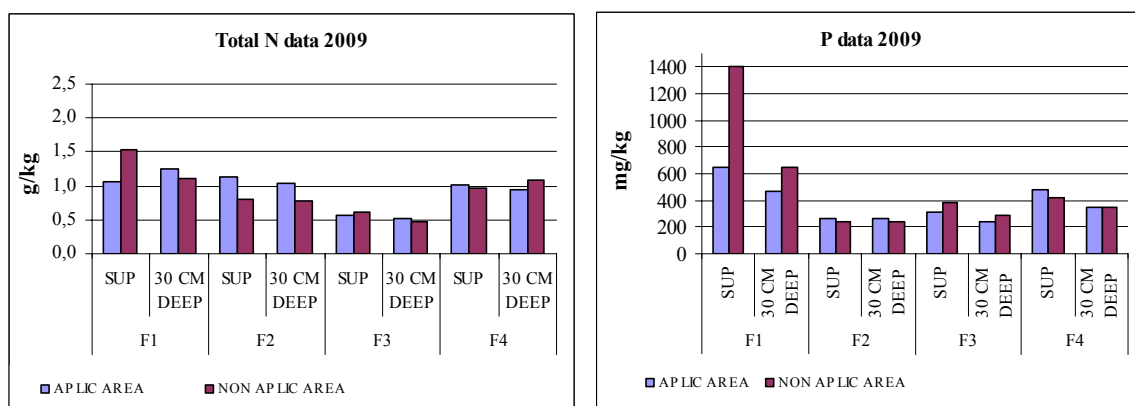
**Figure 2. Graphic representation of total N and P₂O₅ soil data values in mg/kg, obtained for topsoil and subsoil samples collected in 2009.**

**Table 5. Summary of textural classes for soil samples.**

| Farmer | Topsoil sample | Depth of 30 cm sample |
|--------|----------------|------------------------|
| F1 | Silt-loam/Clay-loam | Clay-loam |
| F2 | Silt-clay | Silt-clay |
| F3 | Loamy-sand | Loamy-sand |
| F4 | Silt-clay | Silt-clay |

confirm they are heavy-textured soils that have low permeability and promote low rates of decomposition; then high application rates of manure on heavy-textured soil may be beneficial because of the high nutrient-holding capacity of these soils. It is possible to appreciate that F3 presents low value for both parameters (N and P), due the coarse-textured soils that are highly permeable and promote rapid decomposition of manure. High application rates of manure to coarse-textured soil may contaminate groundwater through the leaching of nutrients (Vanderholm 1975). However, information on the effects of hog manure on soil physical properties is limited. When slurry data are studied (Table 2 and 4) they show that the composition of analysed samples is different for 2009 as compared to 2008, what can be explained by changes that occur from one year to another in handling, animal feeding and cleaning of facilities. These changes are related to several circumstances (economical situation, weather conditions, sanitary conditions, etc.). However, the amount of nutrients in soils seems not to be influenced by slurry composition.

**Conclusions**

Hog manure should be regarded as a resource, and its management and utilization should be approached accordingly. Application to cropland is one of the most obvious methods of recycling plant nutrients. Soil suitability for hog manure application is a national and international issue. The common method of determining application rates is currently based on the capacity of the crops to take up the nutrients, most often on the N requirement for the selected crop. Plant nutrients removed from the soil in the harvested product fed to the animals are then returned in part to the soil as manure. An effective and easily achievable strategy to reduce the slurry pig accumulation is to apply to on agricultural soils, but it is important to take in account their characterization and valorisation before application.

**References**

Andrades M (1996). 'Prácticas de edafología y climatología'. (Universidad de La Rioja).

Bower CA, Wilcox LV (1965) Soluble salts. In 'Methods of Soils Analysis. Part 2'. (Ed CA Black) pp. 933-940. (American Society of Agronomy Inc.: Madison, WI).

Duchaufour Ph (1970) 'Precis de Pedologie'. (Masson: Paris).

Peech M (1965) Hidrogen-ion activity. In 'Methods of Soils Analysis. Part 2'. (Ed CA Black) pp. 914-916. (American Society of Agronomy Inc.: Madison, WI).

Porta J, López-Acevedo M, y Roquero C (1.999) 'Edafología para la agricultura y el medio ambiente. 2ª Edición'. (Ediciones Mundi-Prensa).

RD 324/2000, de 30 de abril.BOE: Ordenación de las explotaciones porcinas.

Pries J (1996) 'Manure Management Symposium Proceedings'. (Winnipeg: MB).

Vanderholm DH (1975) Nutrient losses from livestock waste during storage, treatment and handling. In 'Managing Livestock Wastes, Proc. 3rd Int. Symposium on Livestock Wastes, Urbana-Champaign' pp. 282-285. (Am. Soc. Agric. Eng.: St. Joseph, Mich).

# Risk assessment of heavy metal contaminated soils with reference to aging effect

Junta Yanai[A, C], Kei Yamada[A], Hidekazu Yamada[A] and Takashi Kosaki[B]

[A]Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Japan.
[B]Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Japan.
[C]Corresponding author. Email yanai@kpu.ac.jp.

## Abstract

To estimate the effect of aging on the availability of heavy metals in soil, relationships between availability of metals in soil and period after contamination were investigated for a range of soils and metals. Five metals, Ni, Cu, Zn, Cd and Pb, were added as nitrate solution (2.5 mmol/kg: single or mixed, or 3 times of their background levels) to four soil samples with various chemical properties: dune soil, alluvial soil, red soil and volcanic soil. The soils were incubated at field capacity for 1day, 1 week, 2 weeks, 4 weeks or 6 months, and exchangeable and available fractions of the metals extracted with 1 $M$ ammonium acetate and 0.005 $M$ DPTA solution (pH 6), respectively, were determined by ICP-AES. The amounts of the metals in available fractions were generally in the order of Cu=Pb < Ni=Zn < Cd. Availability of the metals was in the order of volcanic soil < red soil < alluvial soil < dune soil. Temporal decrease of the metal availability, i.e. aging, was evident for all soils and metals, especially for red soil with high amount of oxides, and the changes became <3% / week after 4 weeks. These results enable us to understand natural attenuation of metal contamination and also to assess the risk of soil contamination by determining available fractions of metals in 4-week incubated soils after artificial contamination.

## Key Words

Aging, availability, contamination, heavy metals, risk assessment, soil.

## Introduction

Soil contamination with heavy metals has been a big issue worldwide (Alloway 1995; Nriagu 1996). It has been carried out intensively to investigate contaminated soils for evaluating the level of contamination in relation to human health and/or environmental conservation. It is also very important to investigate the process of soil contamination itself with special attention to available fractions because it directly relates to the management and prevention of soil contamination. It is generally known that availability of metals in soil decreases with time after contamination (Barrow 1998; Christensen 1984; Lock and Janssen 2003; Lu *et al.* 2005; Lim *et al.* 2002). This phenomenon known as "aging", however, has not been investigated comprehensively for a variety of soils with a range of metals. Based on this background, the objectives of this study were: 1) to investigate the aging effect of metals in soil with reference to the type of soils and metals, and 2) to propose a rational method to assess the risk of soil contamination by taking aging effect into account.

## Methods

### Soil samples

Four kinds of soil samples with variable physico-chemical properties were collected in Japan and used in this experiment: dune soil, alluvial soil, red soil and volcanic soil. According to Soil Taxonomy, they were classified as Psamments, Fluvaquents, Udults and Udands, respectively. Their general physico-chemical properties are listed in Table 1.

### Contamination with metals

Five metals, nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb), were selected as heavy metals potentially toxic to the terrestrial ecosystems. They were added as nitrate solution to 4.0 g of soil sample in a 50mL plastic tube. Firstly, to investigate the effect of chemical characteristics of the metals on their availability, same level of metals were added to the soils; i.e. the level of 2.5 mmol/kg was arbitrarily selected, which was equivalent to 3 times of the background level of Ni (*c.* 150 mg/kg). Their nitrate solutions were added either individually or mixed together to the soils to compare mixed contamination with single one. Secondly, to investigate the aging effect on "realistic" level of contamination, the amounts of metals 3 times of their background levels (Bowen 1979) were added to the soils: 150 mg Ni/kg, 90 mg Cu/kg, 270 mg Zn/kg, 1.05 mg Cd/kg and 105 mg Pb/kg, respectively. In both cases, treatment without heavy metal addition was also prepared as a control. All the treatments were duplicated.

**Table 1. General physico-chemical properties of the soil samples.**

| Soil | pH | EC mS/cm | TC % | TN % | C/N | Sand % | Silt % | Clay % | Texture |
|------|-----|------|------|------|------|------|------|------|------|
| Dune soil (D) | 5.6 | 0.06 | 0.76 | 0.06 | 11.8 | 98.5 | 0.8 | 0.7 | S |
| Alluvial soil (A) | 6.0 | 0.06 | 1.39 | 0.14 | 10.2 | 53.0 | 23.9 | 23.0 | CL |
| Red soil (R) | 5.5 | 0.19 | 0.15 | 0.04 | 3.8 | 35.7 | 8.0 | 56.3 | HC |
| Volcanic soil (V) | 5.6 | 0.20 | 7.10 | 0.48 | 14.9 | 41.5 | 34.3 | 24.2 | CL |

| Soil | CEC cmolc/kg | Exchangeable bases (cmolc/kg) | | | | Total content （mg/kg） | | | | |
|------|------|------|------|------|------|------|------|------|------|------|
| | | Ca | Mg | K | Na | Ni | Cu | Zn | Cd | Pb |
| Dune soil (D) | 3.2 | 1.9 | 0.48 | 0.19 | 0.01 | 0.6 | 14.0 | 43.7 | 0.0 | 6.3 |
| Alluvial soil (A) | 13.0 | 7.0 | 1.1 | 0.54 | 0.03 | 19.2 | 43.1 | 108 | 1.1 | 31.8 |
| Red soil (R) | 18.1 | 9.4 | 0.76 | 0.18 | 0.01 | 21.9 | 14.4 | 41.1 | 1.9 | 11.3 |
| Volcanic soil (V) | 37.1 | 13 | 3.5 | 1.4 | 0.09 | 16.4 | 45.1 | 75.9 | 3.8 | 17.0 |

*Soil incubation, soil extraction and determination of metal concentrations*
The soils were watered to reach at the field capacity and incubated for 1day, 1 week, 2 weeks, 4 weeks or 6 months at 25℃. Exchangeable and available fractions of the metals in soils were determined after incubation. Exchangeable fraction was extracted with 40mL of 1*M* ammonium nitrate solution (Symeonides and McRae, 1977), and available fraction was extracted with 20mL of 0.005*M* DPTA solution (pH 6) (Lindsay and Norvel, 1978). Concentrations of the metals in the extracts were determined by ICP-AES (Seiko Instruments Inc., SPS 1500VR).

## Results and discussion
*Exchangeable and available fractions of the metals under single contamination*
Rates of extraction of available fraction were higher than those of exchangeable fraction, as shown in Figure 1, reflecting the extractability of the solutions used. For both exchangeable and available fractions, rates of extraction were in the order of volcanic soil << red soil < alluvial soil < dune soil. This trend, especially clear for exchangeable fraction, would be due to highly reactive Al and Fe oxides in volcanic soil and red soil. Among metals, rates of extraction were in the order of Cu=Pb < Zn=Ni < Cd, reflecting their intrinsic chemical reactivity in soil. Temporal trend of the exchangeable and available fractions were also observed for all the five metals. In exchangeable fraction, there were sharp decline during the first 4 weeks of incubation and the decrease became rather slight after the period, even though the trend continued longer for Red soil. In available fraction, temporal decline of the rate of extraction continued slightly longer except for volcanic soil. It was concluded that decreasing trend of availability, i.e. aging, was clearly observed in both exchangeable and available fractions.

*Exchangeable and available fractions of the metals under mixed contamination*
In the case of mixed or multiple contaminations, similar patterns were observed as in the case of single contamination. General trend among metals and soils were quite similar but the rates of extraction of the mixed contamination were slightly higher than those of the single contamination. Figure 2 shows the relationship between the rates of extraction of the single and mixed contamination for the exchangeable and available fractions. It is clear that the rates of extraction of the mixed contamination were higher than those of the single contamination, especially for exchangeable fraction, in which the rates were relatively high for red soil and dune soil in terms of soil, and for Pb and Cu in terms of metals. In conclusion, mixed contamination enhanced the risk of soil contamination with metals compared with single contamination, especially for the exchangeable fraction.

*Establishment of the risk assessment of heavy metal contaminated soils with reference to aging effect*
Similar to the case of the same level of metal contamination, rates of extraction of the "realistic" soil contamination were in the order of volcanic soil, red soil < alluvial soil, dune soil (data not shown). Among metals, rates of extraction were in the order of Cu=Pb=Cd < Zn=Ni, reflecting relatively low concentration of Cd in soil. In this case, the period of time for the rate of aging (decrease of rate of extraction) to become < 3% / week was 4 weeks for any soil and for any metal. These results suggest that rate of extraction after artificial metal contamination can be assessed reasonably well after 4 week incubation, by taking aging effect into account. It was concluded, therefore, that risk assessment of soil contamination can be accomplished by the determination of exchangeable or available fraction of soil after 4 weeks incubation of soils artificially spiked with a metal equivalent to 3 times of the background level.
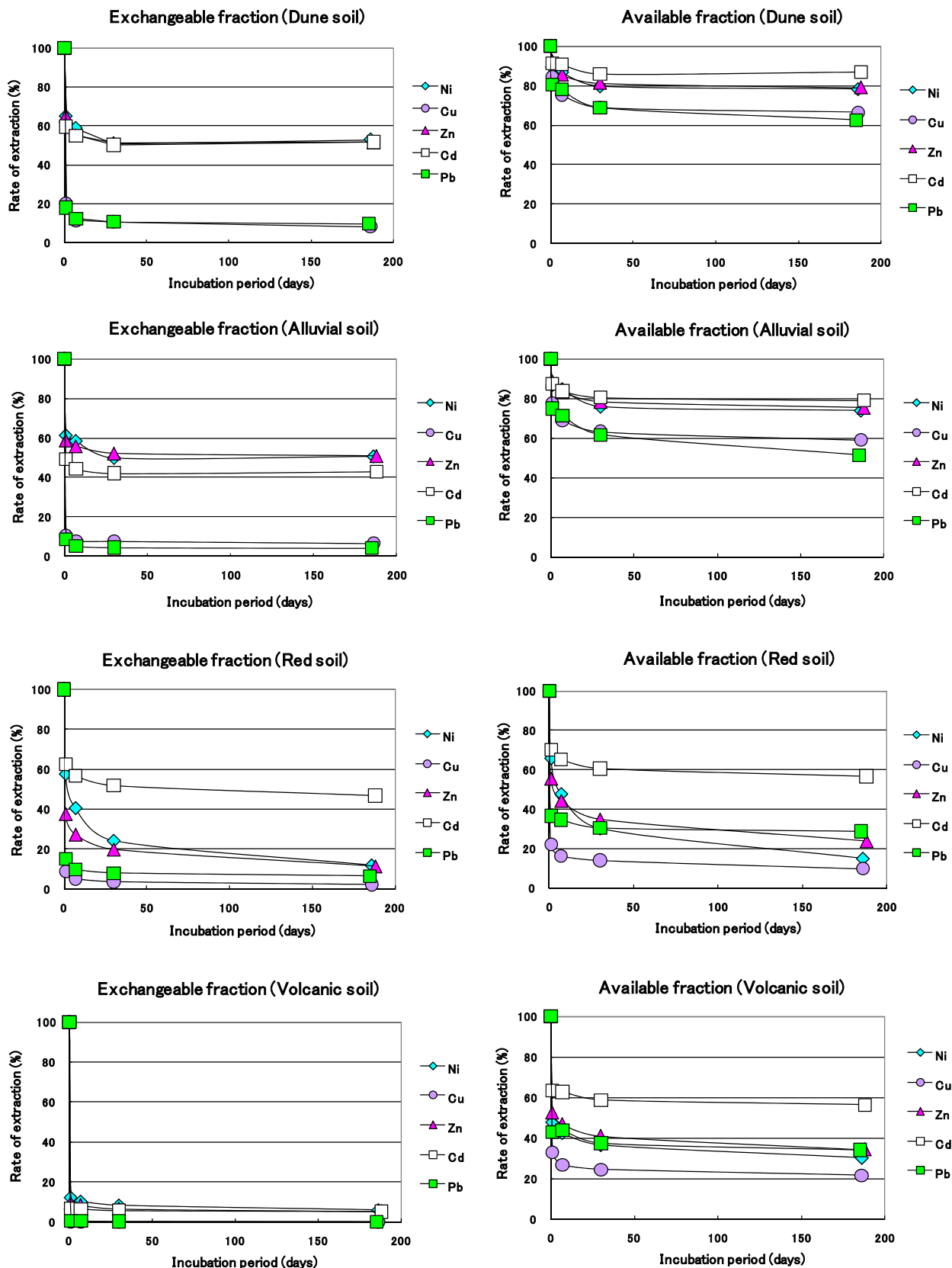
**Figure 1. Temporal change of exchangeable and available fractions of the five metals in four soil samples investigated (single contamination).**

© 2010 19th World Congress of Soil Science, Soil Solutions for a Changing World

1 – 6 August 2010, Brisbane, Australia.  Published on DVD.

57
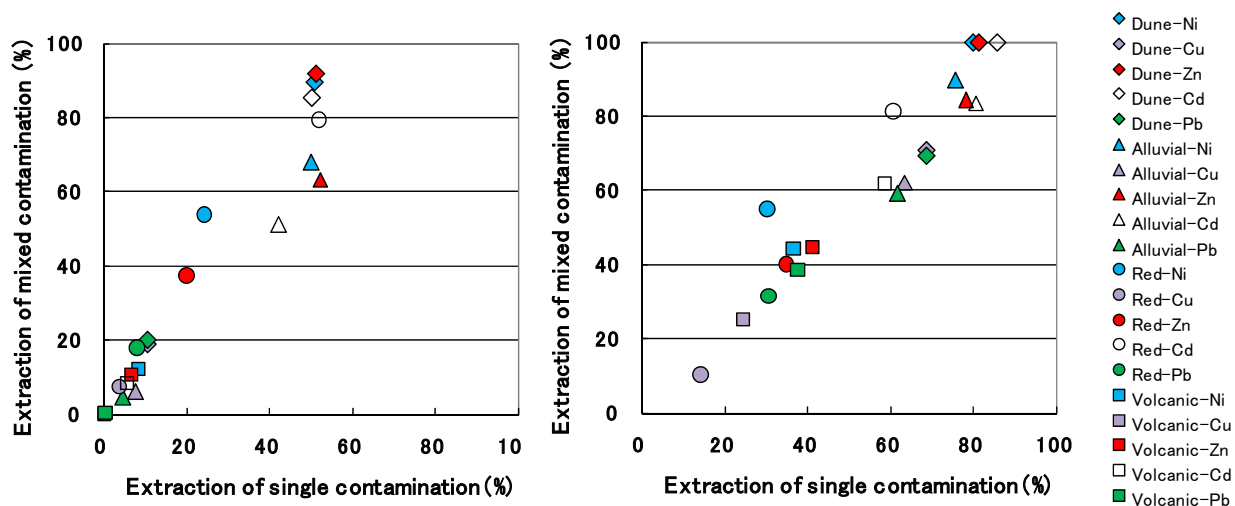
**Figure 2. Relationship between the rates of extraction of the metals of the single and mixed contamination for the exchangeable (left) and available (right) fractions.**

## Conclusion

Effect of type of metals and soils on the metal availability in soil was clearly observed: Cu=Pb < Ni=Zn < Cd for metals and volcanic soil < red soil < alluvial soil < dune soil for soils. Mixed contamination considerably increased metals in exchangeable fraction, especially Pb and Cu, compared with single contamination. Natural attenuation of the metal availability, i.e. aging, was also evident for all soils and the changes generally became <3% / week after 4 weeks. These results enable us to assess contamination risk of soil contamination *prior to* contamination by assessing available fractions of metals in 4-week incubated soils after artificial contamination.

## Acknowledgements

## References

Alloway BJ (1995) 'Heavy Metals in Soils'. (Blackie and Sons Limited: London).

Barrow NJ (1998) Effects of time and temperature on the sorption of cadmium, zinc, cobalt, and nickel by a soil. *Australian Journal of Soil Research* **36**, 941-50.

Bowen HJM (1979) 'Environmental Chemistry of the Elements'. (Academic Press Inc. Ltd.: London).

Christensen TH (1984) Cadmium soil sorption at low concentrations; I. Effect of time, cadmium load, pH, and calcium. *Water, Air, and Soil Pollution* **21**, 105-114.

Lim TT, Tay, JH, Teh CI (2002) Contamination time effect on lead and cadmium fractionation in a tropical coastal clay. *Journal of Environmental Quality* **30**, 806-812.

Lindsay WL, Norbel WA (1978) Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sciience Society America Journal* **42**, 421-428.

Lock K, Janssen CR (2003) Influence of aging on metal availability in soils. *Reviews of Environmental Contamination and Toxicology* **178**, 1-21.

Lu A, Zhang S, Shan X (2005) Time effect on the fractionation of heavy metals in soils. *Geoderma* **125**, 225-234.

Nriagu, JO (1996) A history of global metal pollution. *Nature* **272**, 223-224.

Symeonides C, McRae SG (1977) The assessment of plant-available cadmium in soils. *Journal of Environmental Quality* **6**,120-123.

# Risk assessment of rare metals contained in soil by geo-environmental risk assessment system (GERAS-1)

Yoshishige Kawabe, Yasuhide Sakamoto, Junko Hara, Junko Nishiwaki and Takeshi Komai

Institute for Geo-resource and Environment, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan, Email y-kawabe@aist.go.jp; sakamoto-yasuhide@aist.go.jp; j.hara@aist.go.jp; junko-nishiwaki@aist.go.jp; takeshi-komai@aist.go.jp@aist.go.jp

## Abstract

The exposure rates, the distribution of exposure paths and the risk level of rare metals (antimony, beryllium, barium and vanadium) contained in soil and ground water in Japan have been evaluated by using an originally developed risk assessment model (GERAS-1). The major exposure pathway of these rare metals is the ground water intake. In the case of beryllium and barium, humans also intake them from direct ingestion of soil. The exposure rates and risks were not high for people living in the general environment. The soil contents of the rare metals for the exposure limits are estimated at the following levels: antimony, 34 mg/kg; beryllium, 220 mg/kg; barium, 14000 mg/kg; vanadium, 240 mg/kg.

## Key Words

Risk assessment, exposure model, rare metals, soil contamination.

## Introduction

Rare metals such as antimony, beryllium, barium and vanadium are widely used for alloy material or electronic devices. Since these materials are easily discarded in landfills or in the subsurface environment, there is a possibility that humans are exposed to these rare metals. Risk and exposure assessment for soil and ground water are important for both aspects for health and environmental protection, as well as making proper decisions about remediation done by engineering activities. Exposure due to hazardous chemicals in the subsurface environment is essential to assess risk level for individual people, especially exposure from the soil and ground water. The exposure assessment model plays an essential role for estimating the exposure or risk level for humans. There are three kinds of exposure models to determine the level and distribution of exposure to individuals: One is screening type model. Two is a site-specific type exposure model. And three is a multimedia type exposure model (Komai, 2002). Because the screening type model is the first step in evaluating the risk level of contamination, it is important to develop it in accordance with the categories and properties of chemicals, and the situation and factors specific to Japan. We have developed the screening type of risk assessment model (Geo-environmental Risk Assessment System; GERAS-1) (Kawabe *et al.* 2003, 2005).

In this study, the exposure rates, the distribution of exposure paths and the risk level of rare metals (antimony, beryllium, barium and vanadium) contained in soil and ground water in Japan have been evaluated by using GERAS-1.

## Methods

The risk assessment model used in this study is the geo-environmental risk assessment model for heavy metals (Kawabe *et al.* 2003). It considers both soil properties and exposure factors specific to Japanese situations. In this model the following exposure paths are considered: Ingestion of soil; dermal contact of soil; inhalation of soil; inhalation of indoor air; inhalation of outdoor air; ingestion of ground water; and ingestion of crops (Figure 1).

To input the soil concentration of the rare metals, the cocentrations of rare metals in the pore water and soil air are calculated. Then the concentration of each media, i.e. crops, ground water, indoor or outdoor air, is calculated. Finally, the exposure rates from each path are estimated and then risk is evaluated.

The soil used in GERAS-1 was a loamy sand, which has a high organic carbon content and is a humid soil. The lifetime exposure duration was assumed to be 365 days/year for 70 years (childhood years: 6 years; adult years: 64 years). The body weights of child and adult were 15 kg and 50 kg, respectively. The inhalation rates were 6 $m^3$/day for a child and 15 $m^3$/day for an adult, obtained from the estimation using Travis's equation (Travis, 1987). Drinking water intake rates (1 liter/day for a child and 2 liters/day for an adult) and the soil ingestion rates (200 mg/day for a child and 100 mg/day for an adult) were used for the evaluation. The other parameters such as chemical properties have been described in the literature (Kawabe *et al.* 2003).

The endpoints of risk used in this study were the values of the oral reference dose (RfD).
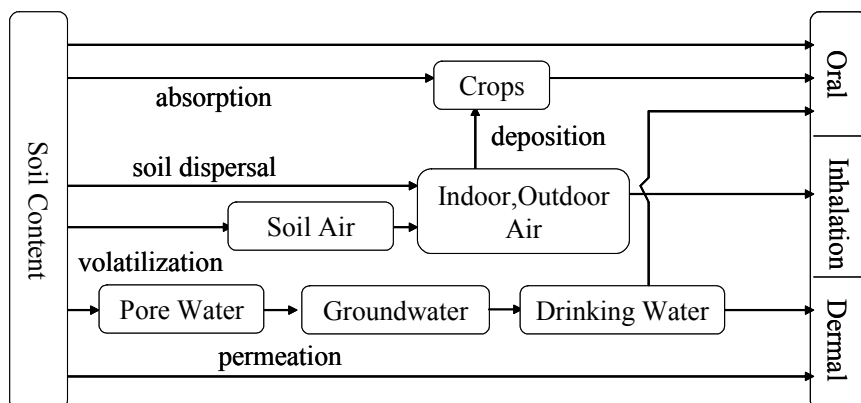


**Figure 1. Exposure paths of chemical substance considered in geo-environmental risk assessment model.**

### Results and discussions

Figure 2 shows the exposure rates and contribution of the different exposure paths during a lifetime (aged 0 to 70) by using GERAS-1. The major exposure pathway is the ground water intake for all rare metals (antimony, 80.4 %; beryllium, 58.3 %; barium, 34.3 %; vanadium, 77.7%). These results indicate that these rare metals easily migrate and are transported to ground water. In the case of beryllium and barium, humans are also exposed to these metals from the direct ingestion of soil (beryllium, 32.4 %; barium, 60.2 %).
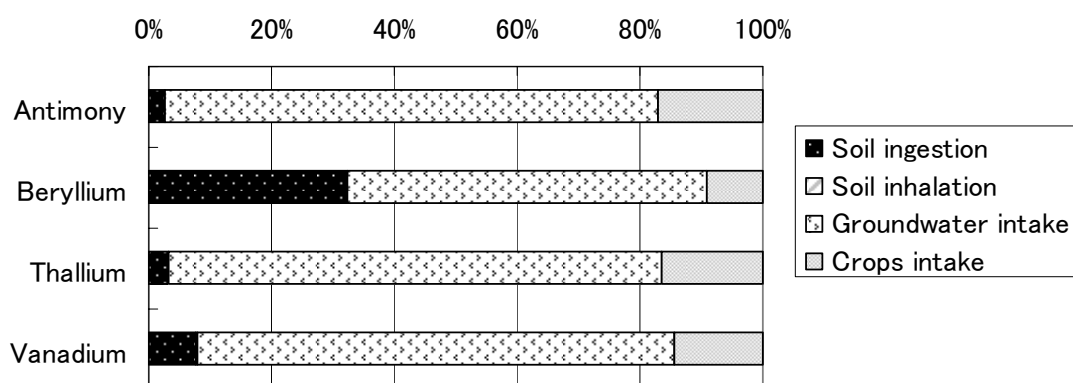


**Figure 2. Exposure pathways of rare metals calculated by the GERAS-1.**

There are no criteria for soil content of these rare metals. To understand the range of the exposure rates and risks, we estimated exposure rates and risks, assuming that the soil content of these rare metals were Clarke number which is the percent by mass for all elements in the earth surface. Table 1 shows the result of this estimation. The total lifetime exposure rate of antimony is calculated at $5.9 \times 10^{-2}$ µg/kg/day, which corresponds to about 1.0 % of the oral reference dose (RfD).

**Table 1.  Exposure rates and remediation goal of rare metals, when the soil content of these rare metals were the Clarke number.**

| Rare metals | | Antimony | Beryllium | Barium | Vanadium |
|---|---|---|---|---|---|
| Clarke number [%] | | 0.00005 | 0.0006 | 0.023 | 0.015 |
| Lifetime exposure rate [µg/kg/day] | Ingestion of soil | $1.5 \times 10^{-3}$ | $1.8 \times 10^{-2}$ | $6.8 \times 10^{-1}$ | $4.5 \times 10^{-1}$ |
| | Ingestion of groundwater | $4.7 \times 10^{-2}$ | $3.2 \times 10^{-2}$ | $3.9 \times 10^{-1}$ | $4.5 \times 10^{0}$ |
| | Inhalation of soil | $4.8 \times 10^{-6}$ | $5.8 \times 10^{-5}$ | $2.2 \times 10^{-3}$ | $1.4 \times 10^{-3}$ |
| | Crops intake | $1.0 \times 10^{-2}$ | $5.1 \times 10^{-3}$ | $6.1 \times 10^{-2}$ | $8.33 \times 10^{-1}$ |
| | Total | $5.9 \times 10^{-2}$ | $5.5 \times 10^{-2}$ | $1.1 \times 10^{0}$ | $5.7 \times 10^{0}$ |
| Oral RfD [µg/kg/day] | | 0.4 | 2 | 200 | 9 |
| Total/RfD [%] | | 1.0 | 2.8 | 0.6 | 64 |
| Remediation goal [mg/kg-soil] | | 34 | 220 | 14000 | 240 |

According to an estimate by our model, soil content of antimony should be around 34 mg/kg. In the case of the other rare metals, total lifetime exposure rates did not exceed RfD. These results suggest that these rare metals have a low risk for humans living in the general environment. According to an estimate by our model, soil contents of beryllium, barium and vanadium should be around 220 mg/kg, 14,000 mg/kg and 240 mg/kg, respectively.

**Conclusion**

Risk based assessment makes it possible for a quantitative analysis of environmental risk for health and ecology as well as a cost-effectiveness analysis and a socio-economical analysis. In this study, the exposure rates, the distribution of exposure paths and the risk level of rare metals contained in soil and ground water in Japan have been evaluated by using an originally developed risk assessment model (GERAS-1). Further, research dealing with exposure to the subsurface environment and its risk assessment has just started in Japan.  Therefore, many factors and parameters, such as soil properties or exposure factors for the assessment, are needed.

**References**

Komai T (2002) Methodology of exposure assessment of contaminated soil and groundwater. *Journal of Chemical Engineers* **41**, 127-132.

Kawabe Y, Komai T, Sakamoto Y (2003) Exposure estimation of heavy metals in Japan, risk analysis by geo-environmental risk assessment Model. *Journal of MMIJ* **119**, 427-433.

Kawabe Y, Komai T, Sakamoto Y (2005) Exposure estimation of organic compounds in Japan, risk analysis by geo-environmental risk assessment model, *Journal of MMIJ* **121**, 19-27.

Travis CC (1987) Drinking Water and Health, Volume 8 (National Academy of Sciences, Washington, DC.), pp. 208-220.

# Soil loss calculations with WEPP and USLE models on sloping arable land near Isaszeg, Hungary

Krisztina Demény[A,C], Csaba Centeri[A] and Gergely Jakab[B]

[A]Department of Nature Conservation and Landscape Ecology, Institute of Environmental and Landscape Management, Faculty of Agricultural and Environmental Sciences, Szent István University, 2103-Gödöllő, Páter K. u. 1, Hungary, Email Centeri.Csaba@kti.szie.hu
[B]Research Institute of Geography, Hungarian Academy of Sciences, H-1112-Budapest, XI. Budaörsi ut 45, Hungary, Email jakab@sparc.core.hu
[C]Budapest Tech Polytechnical Institute Rejtő Sándor, Faculty of Light Industry and Environmental Protection Engineering, H-1034 Budapest, Doberdó út 6, Hungary, E-mail demeny.krisztina@rkk.bmf.hu

## Abstract

The global economical crisis forced all farmers to increase cost effectiveness on their farms. Soil loss calculations provide important information because losing soil means losing nutrients that are expensive not only to buy but also to spread and work into the soil. The examined area has a loessy sand parent material. Intensive arable farming, high compaction and small infiltration rate result in high erodibility. WEPP and USLE model were chosen to be used to provide information from various sources and also to compare the efficiency of the models on a slope of intensive arable farmland. The results show that on the upper and middle slope sections WEPP calculates more soil loss than USLE while at the bottom of the slopes WEPP calculates much more than USLE. On-site investigations proved that the lower part of the slope is sedimented, so USLE is closer to reality at the bottom of the slope.

## Key Words

Soil erosion, modelling, soil loss, WEPP, USLE, intensive farming.

## Introduction

Soil loss reaches smaller extents in Hungary than in tropical countries, but still remains an ongoing problem on agricultural fields of Hungary. The phenomenon is examined mainly in hilly areas or in medium size mountainous outskirts of Hungary, where precipitation is reaching 800 mm /year. In the Isaszeg area the amount of precipitation (600mm/y) and its intensity is not extremely high but the determining parent material (sand mixed with loess) resulted in high erodibility and on arable farms soil loss can reach higher proportion that is causing economical loss for the farmers and for local communities through cleaning up off site effects. Around Isaszeg gullies are wide spread, covering 11.19ha of the outskirts of the settlement. The crop rotation contains a high percentage of of sunflower and maize and thus does not support soil protection measures (Centeri 2002, Szilassi *et al.* 2006). Better management needs to be achieved for a more sound nature and environmental protection (Jordan *et al.* 2005). Soil and nutrient loss are calculated in erosion models all over the world (Gournellos *et al.* 2004, Pimentel *et al.* 1995, Renwick *et al.* 2008, Gordon *et al.* 2008, Rhoton et al 2008, Montgomery 2007, Vanacker *et al.* 2007), especially in connection with arable cultivation.

## Methods

The well-known USLE (Wischmeier and Smith 1978) and WEPP (Flanagan models were used for the analyses. The Water Erosion Prediction Project (WEPP) was started in 1985. Its purpose was to develop new-generation water erosion prediction technology, originally (as well as the USLE) for use in the USA. The WEPP model was developed by the USDA-ARS to replace empirically based erosion prediction technologies, such as USLE, RUSLE, MUSLE. The WEPP model simulates many of the formerly missing physical processes important in soil erosion (e.g. infiltration, runoff, raindrop and flow detachment, sediment transport, deposition, plant growth, and residue decomposition) as input parameters. The WEPP project is similar to USLE because it was constructed based on extensive field experimental program (on cropland, rangeland and disturbed forest sites). The model can be used with Microsoft Windows operating system graphical interfaces, web-based interfaces, and integration with Geographic Information Systems since 1995. Watershed channel and impoundment components, CLIGEN weather generator, the daily water balance and evapotranspiration routines, and the prediction of subsurface lateral flow along low-permeability soil layers was developed and continuously improved (Chaves and Nearing 1991; Risse *et al.* 1994; Flanagan *et al.* 2007; Deer-Ascough *et al.* 1995; Grismer 2007; Moffet *et al.* 2007; Kim *et al.* 2007; Bonilla *et al.* 2007; Moore *et al.* 2007, Shen *et al.* 2009). Input parameters for the WEPP model: rainfall (amount 16.50 mm,

duration 48 min), normalized peak intensity (2.73), normalized time to peak (0.15). Land use was tilled fallow. Slope length and slope angle was calculated based on the topography map of the area and on in situ check with GPS. Input parameters for the USLE model were as it is detailed in Table 1 with the results of soil loss calculations.

## Results

The results of soil loss calculations with USLE model for the selected slope section of the Isaszeg arable field can be found in Table 1.

**Table 1. Input parameters and results of the simulation with the USLE model, Isaszeg, Hungary.**

| Slope section | $R^A$ | K | L | S | A (t/ha) | A (kg/ha) | A (kg/m²) |
|---|---|---|---|---|---|---|---|
| Upper_01 | | 0.38 | 0.52 | 0.57 | 1.37 | 1366.09 | 0.136609 |
| Upper_02 | 12,12882 | 0.28 | 1.27 | 1.33 | 5.74 | 5736.30 | 0.573630 |
| Middle | | 0.009 | 1.515 | 1.95 | 0.32 | 322.48 | 0.032248 |
| Lower | | 0.0001 | 1.41 | 0.57 | 0.00 | 0.97 | 0.000097 |

[A]in this special case, since the calculation is for one rainfall event, this is erosivity index, C and P factors = 1

The results of soil loss calculations with WEPP model can be found in Tables 2-5.

**Table 2. Results of the simulation with the WEPP model for the upper slope third No.1, Isaszeg, Hungary.**

| $PD^A$ (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) |
|---|---|---|---|---|---|---|---|---|---|
| 0.06 | 0.012 | 1.39 | 0.012 | 2.73 | 0.012 | 4.06 | 0.037 | 2.60 | 0.012 |
| 0.12 | 0.012 | 1.45 | 0.012 | 2.79 | 0.012 | 4.12 | 0.039 | 2.66 | 0.012 |
| 0.18 | 0.012 | 1.51 | 0.012 | 2.85 | 0.012 | 4.18 | 0.041 | 3.94 | 0.033 |
| 0.24 | 0.012 | 1.57 | 0.012 | 2.91 | 0.012 | 4.24 | 0.043 | 4.00 | 0.035 |
| 0.30 | 0.012 | 1.64 | 0.012 | 2.97 | 0.012 | 4.30 | 0.045 | 5.27 | 0.076 |
| 0.36 | 0.012 | 1.70 | 0.012 | 3.03 | 0.012 | 4.36 | 0.047 | 5.33 | 0.078 |
| 0.42 | 0.012 | 1.76 | 0.012 | 3.09 | 0.012 | 4.42 | 0.049 | 5.39 | 0.080 |
| 0.48 | 0.012 | 1.82 | 0.012 | 3.15 | 0.012 | 4.48 | 0.051 | 5.45 | 0.081 |
| 0.55 | 0.012 | 1.88 | 0.012 | 3.21 | 0.012 | 4.54 | 0.053 | 5.51 | 0.083 |
| 0.73 | 0.012 | 1.94 | 0.012 | 3.27 | 0.012 | 4.60 | 0.055 | 5.57 | 0.085 |
| 0.79 | 0.012 | 2.00 | 0.012 | 3.33 | 0.012 | 4.66 | 0.057 | 5.63 | 0.087 |
| 0.85 | 0.012 | 2.06 | 0.012 | 3.39 | 0.014 | 4.72 | 0.059 | 5.69 | 0.089 |
| 0.91 | 0.012 | 2.12 | 0.012 | 3.45 | 0.016 | 4.78 | 0.061 | 5.75 | 0.090 |
| 0.97 | 0.012 | 2.18 | 0.012 | 3.51 | 0.018 | 4.84 | 0.063 | 5.81 | 0.092 |
| 1.03 | 0.012 | 2.24 | 0.012 | 3.57 | 0.020 | 4.91 | 0.065 | 5.87 | 0.094 |
| 1.09 | 0.012 | 2.30 | 0.012 | 3.63 | 0.023 | 4.97 | 0.067 | 5.94 | 0.096 |
| 1.15 | 0.012 | 2.36 | 0.012 | 3.69 | 0.025 | 5.03 | 0.069 | 6.00 | 0.097 |
| 1.21 | 0.012 | 2.42 | 0.012 | 3.75 | 0.027 | 5.09 | 0.070 | 6.06 | 0.099 |
| 1.27 | 0.012 | 2.48 | 0.012 | 3.82 | 0.029 | 5.15 | 0.072 | | |
| 1.33 | 0.012 | 2.54 | 0.012 | 3.88 | 0.031 | 5.21 | 0.074 | | |

[A]PD = Profile distances are from top to bottom of hillslope, SOL = Soil loss

**Table 3. Results of the simulation with the WEPP model for the upper slope third No.2., Isaszeg, Hungary.**

| $PD^A$ (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) | PD (m) | SOL (kg/m²) |
|---|---|---|---|---|---|---|---|---|---|
| 6.42 | 0.107 | 13.62 | 0.201 | 20.82 | 0.280 | 28.02 | 0.350 | 35.22 | 0.283 |
| 6.78 | 0.112 | 13.98 | 0.205 | 21.18 | 0.284 | 28.38 | 0.349 | 35.58 | 0.278 |
| 7.14 | 0.117 | 14.34 | 0.209 | 21.54 | 0.288 | 28.74 | 0.346 | 35.94 | 0.275 |
| 7.50 | 0.122 | 14.70 | 0.213 | 21.90 | 0.291 | 29.10 | 0.344 | 36.30 | 0.277 |
| 7.86 | 0.127 | 15.06 | 0.218 | 22.26 | 0.295 | 29.46 | 0.341 | 36.66 | 0.279 |
| 8.22 | 0.132 | 15.42 | 0.222 | 22.62 | 0.298 | 29.82 | 0.339 | 37.02 | 0.282 |
| 8.58 | 0.137 | 15.78 | 0.226 | 22.98 | 0.302 | 30.18 | 0.336 | 37.38 | 0.284 |
| 8.94 | 0.142 | 16.14 | 0.230 | 23.34 | 0.306 | 30.54 | 0.333 | 37.74 | 0.286 |
| 9.30 | 0.147 | 16.50 | 0.234 | 23.70 | 0.309 | 30.90 | 0.330 | 38.10 | 0.288 |
| 9.66 | 0.151 | 16.86 | 0.238 | 24.06 | 0.313 | 31.26 | 0.327 | 38.46 | 0.291 |
| 10.02 | 0.156 | 17.22 | 0.242 | 24.42 | 0.316 | 31.62 | 0.323 | 38.82 | 0.293 |
| 10.38 | 0.161 | 17.58 | 0.246 | 24.78 | 0.320 | 31.98 | 0.320 | 39.18 | 0.295 |
| 10.74 | 0.165 | 17.94 | 0.250 | 25.14 | 0.323 | 32.34 | 0.316 | 39.55 | 0.297 |
| 11.10 | 0.170 | 18.30 | 0.254 | 25.50 | 0.326 | 32.70 | 0.313 | 39.91 | 0.299 |
| 11.46 | 0.174 | 18.66 | 0.258 | 25.86 | 0.330 | 33.06 | 0.309 | 40.27 | 0.301 |
| 11.82 | 0.179 | 19.02 | 0.261 | 26.22 | 0.333 | 33.42 | 0.305 | 40.63 | 0.304 |
| 12.18 | 0.183 | 19.38 | 0.265 | 26.58 | 0.337 | 33.78 | 0.301 | 40.99 | 0.306 |
| 12.54 | 0.188 | 19.74 | 0.269 | 26.94 | 0.340 | 34.14 | 0.297 | 41.35 | 0.308 |
| 12.90 | 0.192 | 20.10 | 0.273 | 27.30 | 0.343 | 34.50 | 0.292 | 41.71 | 0.310 |
| 13.26 | 0.196 | 20.46 | 0.276 | 27.66 | 0.347 | 34.86 | 0.288 | 42.07 | 0.312 |

[A]PD = Profile distances are from top to bottom of hillslope, SOL = Soil loss

**Table 4.  Results of the simulation with the WEPP model for the middle slope third, Isaszeg, Hungary.**

| PD[A] (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) |
|---|---|---|---|---|---|---|---|---|---|
| 42.57 | 0.189 | 52.76 | 0.177 | 62.94 | 0.165 | 73.12 | 0.153 | 83.30 | 0.198 |
| 43.08 | 0.189 | 53.26 | 0.176 | 63.45 | 0.165 | 73.63 | 0.154 | 83.81 | 0.197 |
| 43.59 | 0.188 | 53.77 | 0.176 | 63.95 | 0.164 | 74.14 | 0.158 | 84.32 | 0.196 |
| 44.10 | 0.187 | 54.28 | 0.175 | 64.46 | 0.163 | 74.64 | 0.162 | 84.83 | 0.195 |
| 44.61 | 0.187 | 54.79 | 0.175 | 64.97 | 0.163 | 75.15 | 0.166 | 85.33 | 0.195 |
| 45.12 | 0.186 | 55.30 | 0.174 | 65.48 | 0.162 | 75.66 | 0.170 | 85.84 | 0.194 |
| 45.63 | 0.185 | 55.81 | 0.173 | 65.99 | 0.162 | 76.17 | 0.174 | 86.35 | 0.193 |
| 46.14 | 0.185 | 56.32 | 0.173 | 66.50 | 0.161 | 76.68 | 0.178 | 86.86 | 0.192 |
| 46.65 | 0.184 | 56.83 | 0.172 | 67.01 | 0.160 | 77.19 | 0.181 | 87.37 | 0.192 |
| 47.16 | 0.184 | 57.34 | 0.172 | 67.52 | 0.160 | 77.70 | 0.185 | 87.88 | 0.191 |
| 47.67 | 0.183 | 57.85 | 0.171 | 68.03 | 0.159 | 78.21 | 0.189 | 88.39 | 0.190 |
| 48.17 | 0.182 | 58.36 | 0.170 | 68.54 | 0.159 | 78.72 | 0.193 | 88.90 | 0.190 |
| 48.68 | 0.182 | 58.86 | 0.170 | 69.05 | 0.158 | 79.23 | 0.196 | 89.41 | 0.189 |
| 49.19 | 0.181 | 59.37 | 0.169 | 69.55 | 0.157 | 79.73 | 0.200 | 89.92 | 0.188 |
| 49.70 | 0.181 | 59.88 | 0.169 | 70.06 | 0.157 | 80.24 | 0.202 | 90.42 | 0.187 |
| 50.21 | 0.180 | 60.39 | 0.168 | 70.57 | 0.156 | 80.75 | 0.201 | 90.93 | 0.187 |
| 50.72 | 0.179 | 60.90 | 0.167 | 71.08 | 0.156 | 81.26 | 0.200 | 91.44 | 0.186 |
| 51.23 | 0.179 | 61.41 | 0.167 | 71.59 | 0.155 | 81.77 | 0.200 | 91.95 | 0.185 |
| 51.74 | 0.178 | 61.92 | 0.166 | 72.10 | 0.155 | 82.28 | 0.199 | 92.46 | 0.185 |
| 52.25 | 0.178 | 62.43 | 0.166 | 72.61 | 0.154 | 82.79 | 0.198 | 92.97 | 0.184 |

[A]PD = Profile distances are from top to bottom of hillslope, SOL = Soil loss

**Table 4.  Results of the simulation with the WEPP model for the lower slope third, Isaszeg, Hungary.**

| PD[A] (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) | PD (m) (m) | SOL (kg/m²) |
|---|---|---|---|---|---|---|---|---|---|
| 93.41 | 0.109 | 102.22 | 0.025 | 111.02 | 0.023 | 119.83 | 0.020 | 128.63 | 0.017 |
| 93.85 | 0.109 | 102.66 | 0.025 | 111.46 | 0.022 | 120.27 | 0.020 | 129.07 | 0.017 |
| 94.29 | 0.108 | 103.10 | 0.025 | 111.90 | 0.022 | 120.71 | 0.019 | 129.51 | 0.017 |
| 94.73 | 0.104 | 103.54 | 0.025 | 112.34 | 0.022 | 121.15 | 0.019 | 129.96 | 0.016 |
| 95.17 | 0.098 | 103.98 | 0.025 | 112.78 | 0.022 | 121.59 | 0.019 | 130.40 | 0.016 |
| 95.61 | 0.092 | 104.42 | 0.025 | 113.22 | 0.022 | 122.03 | 0.019 | 130.84 | 0.016 |
| 96.05 | 0.086 | 104.86 | 0.024 | 113.66 | 0.022 | 122.47 | 0.019 | 131.28 | 0.016 |
| 96.49 | 0.080 | 105.30 | 0.024 | 114.10 | 0.022 | 122.91 | 0.019 | 131.72 | 0.016 |
| 96.93 | 0.074 | 105.74 | 0.024 | 114.54 | 0.021 | 123.35 | 0.019 | 132.16 | 0.016 |
| 97.37 | 0.068 | 106.18 | 0.024 | 114.99 | 0.021 | 123.79 | 0.018 | 132.60 | 0.016 |
| 97.81 | 0.062 | 106.62 | 0.024 | 115.43 | 0.021 | 124.23 | 0.018 | 133.04 | 0.015 |
| 98.25 | 0.055 | 107.06 | 0.024 | 115.87 | 0.021 | 124.67 | 0.018 | 133.48 | 0.015 |
| 98.69 | 0.049 | 107.50 | 0.024 | 116.31 | 0.021 | 125.11 | 0.018 | 133.92 | 0.015 |
| 99.13 | 0.043 | 107.94 | 0.023 | 116.75 | 0.021 | 125.55 | 0.018 | 134.36 | 0.015 |
| 99.57 | 0.036 | 108.38 | 0.023 | 117.19 | 0.021 | 125.99 | 0.018 | 134.80 | 0.015 |
| 100.01 | 0.030 | 108.82 | 0.023 | 117.63 | 0.020 | 126.43 | 0.018 | 135.24 | 0.015 |
| 100.46 | 0.026 | 109.26 | 0.023 | 118.07 | 0.020 | 126.87 | 0.017 | 135.68 | 0.015 |
| 100.90 | 0.026 | 109.70 | 0.023 | 118.51 | 0.020 | 127.31 | 0.017 | 136.12 | 0.014 |
| 101.34 | 0.026 | 110.14 | 0.023 | 118.95 | 0.020 | 127.75 | 0.017 | 136.56 | 0.014 |
| 101.78 | 0.025 | 110.58 | 0.023 | 119.39 | 0.020 | 128.19 | 0.017 | 137.00 | 0.014 |

[A]PD = Profile distances are from top to bottom of hillslope, SOL = Soil loss

Comparing the results of USLE (Table 1) and WEPP (Tables 2-5) we can see that USLE calculates more soil loss for the upper third No.1. and No.2. (and No.2. values are closer), while WEPP calculates higher values for the middle slope section. Each model calculates almost no erosion for the lower slope third.

**Conclusion**
We can conclude that in the present situation (with the given input parameters) USLE and WEPP calculated different soil loss values for the upper and middle slope thirds. The importance of local measurements in order to make these models more appropriate is evident in order to provide more precise input parameters

## References

Bonilla CA, Norman JA, Molling CC (2007) Water erosion estimation in topographically complex landscapes: Model description and first verifications. *Soil Science Society of America Journal* **71**, 1524-1537.

Centeri Cs (2002) The role of vegetation cover in soil erosion on the Tihany Peninsula. *Acta Botanica Hungarica* **44**, 285-295.

Chaves HML, Nearing MA (1991) Uncertainty analysis of the WEPP soil erosion model. *Transactions of the ASAE* **34**, 2437-2444.

Deer-Ascough LA, Weesies GA, Ascough II JC, Laflen JM (1995) Plant parameter database for erosion prediction models. *Applied Engineering in Agriculture of ASAE* **11**, 659-666.

Flanagan DC, Gilley JE, Franti TG (2007) Water Erosion Prediction Project (WEPP): Development history, model capabilities, and future enhancements. *Transactions of the ASABE* **50**, 1603-1612.

Gordon LM, Bennett SJ, Alonso CV, Bingner RL (2008) Modeling long-term soil losses on agricultural fields due to ephemeral gully erosion. *Journal of Soil and Water Conservation*, **63**, 173-181.

Gournellos Th, Evelpidou N, Vassilopoulos A (2004) Developing an Erosion risk map using soft computing methods (case study at Sifnos island). *Natural Hazards* **31**, 39-61.

Grismer ME (2007) Soil restoration and erosion control: Quantitative assessment and direction. *Transactions of the ASABE* **50**, 1619-1626.

Jordan Gy, van Rompaey A, Szilassi P, Csillag G, Mannaerts C, Woldai T (2005) Historical land use changes and their impact on sediment fluxes in the Balaton basin (Hungary). *Agriculture, Ecosystems and Environment* **108**, 119-130.

Kim IJ, Hutchinson SL, Hutchinson JMS, Young CB (2007) Riparian ecosystem management model: Sensitivity to soil, vegetation, and weather input parameters. *Journal of the American Water Resources Association* **43**, 1171-1182.

Moffet CA, Pierson FB, Robichaud PR, Spaeth KE, Hardegree SP (2007) Modeling soil erosion on steep sagebrush rangeland before and after prescribed fire. *Catena* **71**, 218-228.

Montgomery DR (2007) Soil erosion and agricultural sustainability. *PNAS* **104**, 13268-13272.

Pimentel D, Harvey C, Resosudarmo P, Sinclair K, Kurz D, McNair M, Crist S, Shpritz L, Fitton L, Saffouri R, Blair R (1995) Environmental and Economic Costs of Soil Erosion and Conservation Benefits. *Science* **267**, 1117-1123.

Renwick WH, Vanni MJ, Zhang Q, Patton J (2008) Water Quality Trends and Changing Agricultural Practices in a Midwest U.S. Watershed, 1994-2006. *J. Environ. Qual.* **37**, 1862-1874.

Rhoton FE, Emmerich WE, DiCarlo DA, McChesney DS, Nearing MA, Ritchie JC (2008) Identification of Suspended Sediment Sources Using Soil Characteristics in a Semiarid Watershed. *Soil Sci. Soc. Am. J.* **72**, 1102-1112.

Risse LM, Nearing MA, Savabi MR (1994) Determining the Green and Ampt effective hydraulic conductivity from rainfall-runoff data for the WEPP model. *Transactions of the ASAE* **37**, 411-418.

Shen ZY, Gong YW, Li YH, Hong Q, Xu L, Liu RM (2009) A comparison of WEPP and SWAT for modeling soil erosion of the Zhangjiachong Watershed in the Three Gorges Reservoir Area. *Agricultural Water Management* **96**, 1435-1442.

Szilassi P, Jordan G, van Rompaey A, Csillag G (2006) Impacts of historical land use changes on erosion and agricultural soil properties in the Kali Basin at Lake Balaton, Hungary. *Catena* **68**, 96-108.

Vanacker V, von Blanckenburg F, Govers G, Molina A, Poesen J, Deckers J, Kubik P (2007) Restoring dense vegetation can slow mountain erosion to near natural benchmark levels. *Geology* **35**, 303-306.

Wischmeier WH, Smith DD (1978) 'Predicting rainfall erosion losses: A guide to conservation planning. U.S. Department of Agriculture. Handbook No. 537'.

# Spatial autoregression model for heavy metals in Beijing cultivated soils

Xiaoni Huo[A,C], Danfeng Sun[A] and Hong Li[B]

[A]Department of Land Resources and Management, College of Natural Resources and Environmental Science, China Agricultural University, Beijing, China, Email hxnsky@126.com, sundf@cau.edu.cn
[B]Beijing Academy of Agriculture and Forestry, Beijing, China, Email lihsdf@sina.com
[C]Department of Environmental Engineering, Taiyuan University, Taiyuan, China

## Abstract
Soil heavy metals may be affected by many influencing factors, in order to find out the important factors leading to pollution in Beijing cultivated soils for risk evaluation and pollution control, the relationship between heavy metals and the influencing factors was analysed. Because of the significant spatial autocorrelation of heavy metals and the influencing factors, the significant positive spatial autocorrelation was detected for the residuals of a standard linear regression model. To consider the spatial autocorrelation fully, a spatial autoregression model was constructed. Taking Cr as an example, the spatial autoregression model for Cr had a better goodness-of-fit than the standard linear regression model, while the spatial autocorrelation of the residuals disappeared, indicating the spatial autoregression model could capture the spatial autocorrelation of data and explain the relationship between heavy metals and their influencing factors excellently. Spatial autoregression model showed that the important controlling factors for Cr in Beijing cultivated soils were soil parent rock and land use intensity.

## Key Words
Spatial autoregression model, heavy metals, cultivated soils, Beijing.

## Introduction
Heavy metals in cultivated soils are controlled by many factors, such as the overuse of fertilizer and pesticides, the mineral resource exploration and industry development. These factors can lead to the excessive accumulation of heavy metals, which may not only result in soil contamination but also affect the groundwater and food chains (Khan *et al.* 2008). Generally, the relationship between heavy metals and these factors analysed with standard statistical models, and the data analysed with the methods should be independent and identically distributed (Cliff and Ord 1981). However, Huo *et al.* (2009a) have showed that heavy metals had significant spatial autocorrelation, which contains some useful information. If the standard statistical models are used, they cannot capture all the spatial autocorrelation characteristics of data. To overcome the defect, Cliff and Ord (1981) provided a spatial autoregression model to deal with spatial data. Recently, the spatial autoregression model has been extensively applied in many studies, but the method is still not used by heavy metal distribtion. Therefore, the objectives of this study were to explore the relationship between heavy metals in Beijing cultivated soils and their influencing factors using a spatial autoregression model, and to find out the important factors for soil heavy metal risk evaluation and pollution control.

## Methods
The study area is Beijing province. A total of 1018 soil samples were collected from Beijing cultivated land in 2006. Huo *et al.* (2009b) have provided the details of the study area, the methods for soil sample processing and analysis and the distribution of soil samples.

### Spatial autoregression model
The most general formulation of a spatial autoregression model is Eq. (1) (Anselin, 1988):

$$y = \rho w_1 y + x\beta + u$$

$$u = \lambda w_2 u + \varepsilon$$

$$\varepsilon \sim N\left(0, \sigma^2 I_n\right) \tag{1}$$

where $y$ is the dependent variable, $x$ is the explanatory variable, $\beta$ is a vector correlated with explanatory variable, $\rho$ is a coefficient of the spatially lagged dependent variable, $\lambda$ is a coefficient of the spatially correlated errors and $w_1$, $w_2$ are spatial weight matrices.
Setting $\rho = \lambda = 0$ produces a standard regression model, without considering spatial autocorrelation characteristics. Setting $\beta = \lambda = 0$ and $\rho \neq 0$ results a first-order spatial autoregression model, showing that the dependent variable is affected by the dependent variable of neighbouring units. Setting $\rho \neq 0$, $\beta \neq 0$ and $\lambda = 0$

produces a mixed regression-spatial autoregression model, indicating that the dependent variable is not only affected by the explanatory variable, but affected by the dependent variable of neighbouring units. This model is also called spatial lagged model. Setting $\beta \neq 0$, $\lambda \neq 0$ and $\rho = 0$ results a spatial error autoregression model. This model indicates that the dependent variable is affected by explanatory variable, dependent variable and explanatory variable of neighbouring units.

*Measures of fit in spatial autoregression model*
In the presence of spatial autocorrelation, the traditional $R^2$ measure of fit is not applicable to the spatial autoregression model. Instead, the so-called pseudo $R^2$ measure can be computed to asses fit. In the standard regression model, the pseudo $R^2$ is equivalent to the $R^2$, but in the spatial autoregression model it is not (Anselin 2002). So, the traditional $R^2$ and the pseudo $R^2$ cannot be compared, but it is possible to compare the pseudo $R^2$ of different spatial models. The measures for goodness-of-fit for the spatial model based on the likelihood function also include the value of the maximised log likelihood (LIK), the Akaike Information Criterion (AIC) and the Schwartz Criterion (SC). The model with the highest LIK, or with the lowest AIC or SC has the best goodness-of-fit. The LIK is not a standardised indicator like $R^2$, so it cannot be interpreted as an absolute value.

*The selection of influencing factors*
Soil heavy metals are affected by both natural processes and anthropogenic activities. All of the factors must be considered fully, while, these data should be obtained and quantified simply. The distance between the cultivated soil and residential area, the distance between the cultivated soil and industrial and mining establishment, the density of road, and the density of different soil types were used to show the effect of residential area, industrial and mining establishment, road, and soil types on heavy metals. The land use intensity was defined by the proportion of fertilizer and pesticide inputs. The land use intensity of orchard land was the strongest, followed by two-crops a year, one-crop a year, and then fallow land. All factors were quantified using geostatistical analyst extension of ArcGis 8.3, and the data were 100×100 m raster data.

**Results**
Table 1 shows the spatial autocorrelation of the residuals presented in the standard linear regression model for Cr, Ni, Zn, and Hg. Although the spatial autocorrelation of the residuals were less than those of heavy metals, they were still significant, thus, it is necessary to select the spatial autoregression model.

**Table 1. Moran's I for soil heavy metals and their residuals of the standard linear regression model.**

| Heavy metals | The Moran's I of heavy metal | The Moran's I of the residuals |
|---|---|---|
| Cr | 0.4801 | 0.3615 |
| Ni | 0.3173 | 0.2689 |
| Zn | 0.2924 | 0.2449 |
| Hg | 0.2725 | 0.1878 |

Taking Cr as an example, Table 2 illustrates the difference between the standard linear regression model and the spatial autoregression model for Cr. Spatial autoregression model 1 contained the same variables as the standard linear regression model. The regressive coefficient of variables in spatial autoregression model 1 were smaller than those in the standard regression model, and the significant of parameters also decreased and some variables were not longer significant ($p < 0.05$), but the LIK of spatial autoregression model was higher than the LIK of the standard linear regression model, indicating that the spatial autoregression model has a better goodness-of-fit. The insignificant variables were dropped from the spatial autoregression model 1 to construct the spatial autoregression model 2. The pseudo $R^2$ and the LIK of the spatial autoregression model 2 decreased slightly, but the parameters were still significant, thus, the difference between the two spatial models was negligible. The Moran's I of the residuals in spatial autoregression model 2 was -0.0565, which tended to 0, indicating the spatial autocorrelation of the residuals disappeared. Thus, the spatial autoregression model could capture the spatial autocorrelation of Cr and the influencing factors and showed the relationship between Cr and the influencing factors.

**Conclusion**
The residuals of the standard linear regression model for Cr, Ni, Zn, and Hg showed significant and positive autocorrelation, indicating that the standard linear regression model failed to consider all the spatial autocorrelation characteristics in the data. Spatial autoregression model for Cr yielded residuals without spatial autocorrelation but with a better goodness-of-fit, while the coefficients of the spatially correlated errors were

**Table 2. The model parameters for three models for Cr.**

| Regression model | Variables | Regression coefficient | Standard error | *t*-test value | *p* |
|---|---|---|---|---|---|
| Standard linear regression model | Constant | 1.7515 | 0.0149 | 117.3316 | 0 |
| | The distance to the residential area | -0.0744 | 0.0245 | -3.0406 | 0.0024 |
| | Land use intensity | 0.0094 | 0.0034 | 2.799 | 0.0052 |
| | The density of haplic fluvo-aquic soil | -0.0113 | 0.0054 | -2.1077 | 0.0353 |
| | The density of aquic-cinnamon soil | -0.0411 | 0.0145 | -2.8453 | 0.0045 |
| | The density of haplic-cinnamon soil | 0.0725 | 0.0168 | 4.3055 | 0 |
| | The density of meadow cinnamon soil | -0.149 | 0.0255 | -5.8497 | 0 |
| | The density of leached drab soil | 0.0329 | 0.014 | 2.3512 | 0.0189 |
| | Measures of fit in standard linear regression model: R2=0.115; LIK=794.474 | | | | |
| Spatial autoregression model 1 | Constant | 1.74 | 0.015 | 117.578 | 0 |
| | The distance to the residential area | -0.004 | 0.021 | -0.193 | 0.847 |
| | Land use intensity | 0.006 | 0.003 | 2.229 | 0.026 |
| | The density of haplic fluvo-aquic soil | 0 | 0.005 | 0.006 | 0.996 |
| | The density of aquic-cinnamon soil | 0.001 | 0.016 | 0.077 | 0.939 |
| | The density of haplic-cinnamon soil | 0.044 | 0.019 | 2.338 | 0.019 |
| | The density of meadow cinnamon soil | -0.037 | 0.027 | -1.367 | 0.172 |
| | The density of leached drab soil | -0.014 | 0.012 | -1.186 | 0.235 |
| | $\lambda$ | 0.66 | 0.031 | 21.61 | 0 |
| | Measures of fit in spatial autoregression model 1: pseudo R2=0.394; LIK=948.943 | | | | |
| Spatial autoregression model 2 | Constant | 1.7427 | 0.0117 | 148.4755 | 0 |
| | Land use intensity | 0.0065 | 0.0028 | 2.2977 | 0.0216 |
| | The density of haplic-cinnamon soil | 0.0452 | 0.0188 | 2.3991 | 0.0164 |
| | $\lambda$ | 0.6631 | 0.0303 | 21.8649 | 0 |
| | Measures of fit in spatial autoregression model 2: pseudo R2=0.392; LIK=946.657 | | | | |

significant ($p<0.05$), indicating that the concentrations of Cr not only were affected by the influencing factors of the own region, but also were affected by the concentrations of heavy metals and influencing factors of the neighbouring regions. The regression coefficient of spatially correlated error was higher than those of the influencing factors, indicating that the concentrations of Cr and influencing factors in the neighbouring regions played an important role for Cr concentrations. Spatial autoregression model showed the important influencing factors for Cr in Beijing cultivated soil were soil parent rock and land use intensity.

**References**

Anselin L (1988) 'Spatial Econometrics: Methods and Models'. (Kluwer Academic Publishers: Dordrech).

Anselin L (2002) Under the hood: Issues in the specification and interpretation of spatial regression models. *Agricultural Economics* **27**, 247-267.

Cliff AD, Ord J K (1981) 'Spatial processes: Models and Applications'. (Pion Ltd: London)

Huo XN, Li H, Sun DF, Zhang WW, Zhou LD, Li BG (2009a) Spatial autocorrelation analysis of heavy metals in cultivated soils in Beijing. *Acta Scientiae Circumstantiae* **29**, 1339-1344.

Huo XN, Li H, Sun DF, Zhou LD, Li BG (2009b) Multi-scale spatial structure of heavy metals in cultivated soils in Beijing. *Environmental Monitoring and Assessment* DOI: 10.1007/s10661-009-0916-7

Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution* **152**, 686-692.

# The role of DTPA and EDDS in remediation of Se from contaminated soil by Brussels sprouts (*Brassica oleracea* var. gemmifera)

Aslıhan ESRİNGÜ Metin TURAN[A]

[A]Ataturk University, Faculty of Agriculture, Department of Soil Science, Erzurum 25240, Turkey, Email esringua@hotmail.com, m_turan25@hotmail.com

## Abstract

The use of plants to remove heavy metals from soil (phytoremediation) is emerging as a cost-effective way compared conventional methods. Because contaminants such as Se, Pb and Cd have limited bioavailability in the soil, methods to facilitate their transport to the stems and roots of plants are required for successful phytoremediation. The objective of this study was to investigate the effects of adding different rates of DTPA (0, 0.5, 1 and 5 mmol/kg of diethylene triamine penta acetate), and EDDS (0, 5, 7.5, and 10 mmol/kg of ethylene daimine dissuccinate) on Se availability in contaminated soils with 0, 5, 10 and 15 mg/kg NaSeO$_4$, on the capacity of *Brussels sprouts* plants to take up Se under a greenhouse conditions. Results indicated that DTPA and EDDS application to Se contaminated soils significantly decreased dry matter yield of plants. Most plant available fractions (water soluble and exchangeable), carbonate, metal oxide, organic matter bound fraction increased linearly with Se application with regression R$^2$ values of 0.90 or greater. At all DTPA and EDDS application rates, Se concentrations in leaves were about 2-3 times higher than in roots and about 3-4 times higher than in stems. Application of DTPA and EDDS over 0.5 and 7.5 mmol/kg doses significantly decreased total Se uptake in leaves, stems, and roots in plants.

## Key Words

EDDS, DTPA, heavy metal availability, phytoextraction, translocation effiviency.

## Introduction

Soil contamination by heavy metals is a global environmental issue due to the rapid development of intensive agriculture and industry in many parts of the world. Elevated concentrations of heavy metals not only lead to reductions in the microbial activity and fertility of the soil and in crop production (McGrath *et al.* 1997), but also threaten human health through the food chain.

The remediation of soil and water contaminated with heavy metals has become a challenging task facing regulators and scientific communities. Contaminated soils can be remediate by physical, chemical and biological techniques (McEldowney *et al.* 1993). Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soils are contaminated. Treatments can be done *in situ* or *ex situ* which are both extremely expensive. These include high temperature treatments, solidifying agents and washing process (USDA and NRCS 2000). Many different remediation methods have been tried to address the rising number of heavy metal contaminated sites. Most of traditional methods are either extremely costly (i.e., excavation, solidification and burial) or simply involve the isolation of the contaminated sites. Some methods, such as soil washing, can pose an adverse effect on biological activity, soil structure and fertility, and incur significant engineering costs. Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soils are contaminated. Unlike conventional methods, phytoremediation is inexpensive, effective, and can be implemented in situ, and it is environmentally friendly. A special advantage of phytoremediation is that soil functioning is maintained and life is the soil is reactivated (Trapp and Karlson 2001).

The solubility of heavy metals in soil is limited due to complexion with organic matter, sorption on clays and oxides, and precipitation as carbonates, hydroxides and phosphates (McBride 1994). Increased solubility of the heavy metal can be achieved by adding synthetic chelants, such as EDDHA [etylenediamine-di (o-hydroxyphenylacetic acid)], EDTA (ethylenediaminetetraacetic acid), and NTA (nitrilotriacetate), and they have been used to enhance the solubility of metals in soils and their subsequent uptake and translocation in plant stems (Huang *et al.* 1997, Kos and Lesˇtan 2003a). Despite the high efficiency of EDTA for inducing the extraction of metals, some concerns have been expressed regarding the enhanced mobility of metals in soil and their potential risks of spreading metal contaminants to groundwater and the surrounding environment due to its high affinity with heavy metals and its poor biodegradability in the environment. EDDS is an easily biodegradable, low-toxic chelant with a strong chemical affinity to Pb, Cu, Se and other

metals. The use of this chelant in the remediation process has received much attention in the past few years (Kos and Lesˇtan 2003b, 2006a).

There is limited information on the use of EDTA and EDDS to enhance Se accumulation in plants. Therefore, this study is carried out to compare the relative efficiency of selected synthetic chelants agents in enhancing Se phytoextraction and to identify soil amendments that increase Se desorption from soil.

**Materials and methods**
A loamy (36.0% sand, 34.0% silt, and 30.0% clay) textured soil was sampled from Erzurum province ($39^o$ 55' N, $41^o$ 61 E) of Turkey. The soil had 1.20% $CaCO_3$, 300.2 mmol/kg $P_2O_5$, 430.3 mmol/kg $K_2O$, 6.90 pH ($H_2O$) and 1.15 dS/m electrical conductivity.
Soil was transferred to 20 cm diameter polyethylene pots. Each soil was treated with 0, 5, 10 and 15 mg/kg $NaSeO_4$ as pollutant. The soil contamination was performed by putting the right amount of heavy metals dissolved in deionised water into each pot (3000 g soil/pot), which was first saturated and then air dried at room temperature and, during this process, the metals in water were thoroughly mixed into the soil. The wetting-drying mixing process was repeated to ensure equilibrium following 1 mo after incubation. To support optimum plant growth 350 N kg ha$^{-1}$ (as ammonium sulfate), 92 kg ha$^{-1}$ P (as triple superphosphate), 166 kg ha$^{-1}$ K (as potassium sulfate) were applied before planting. Three months after the addition of Se, polluted soils were treated with the synthetic chelants agents, DPTA and EDDS, at the rates of 0, 0.5, and 5 mmol/kg of diethylene triamine penta acetate (DTPA), and 0, 5, 7.5, and mmol/kg of ethylene daimine dissuccinate (EDDS). Concentrations of synthetic chelants were based on the upper soil surface layer and were sprayed on the soil surface, following procedures used in a previous work (Vogeler *et al.* 2001).Plants were maintained in a heated greenhouse under natural light at a minimum temperature of 10-11°C and maximum of 25-30°C and a relative humidity of about 30-40%. Day length was 14 h during the experimental period. Plant seeds were germinated for 20 days at 25°C with an approximate of 20.000 plant/ha. Three seedlings were transplanted to each pot containing 3000 g soil. The pots were weighed daily and irrigated with deionised water to replace water lost throughout evapotranspiration. Water content of the soil was adjusted to 70% of field capacity. There were three replicates of each treatment giving a total of 96 pots in a randomized block design. The plants were harvested 150 days after being planted, and soil and plant analyses and Se distribution using a sequential extraction procedure were done according to AOAC (2005), Mertens (2005a), Mertens (2005b) and Tessier *et al.* (1979).
*Statistical analysis:*Each pot was considered as a replicate and all of the treatments were repeated three times. All data were subjected to a two way analysis of variance (ANOVA) and separated by LSD with SPSS 2004.

**Results and discussion**
*Dry matter yield of plants:* Application of the addition of DTPA and EDDS did not impact leaves, stem, root and total dry matter yield of plants without Se contamination in the soils. However, DTPA and EDDS application to Se contaminated soils significantly decreased dry matter yield of plants and plants showed a significant decrease in yield with increase in the DTPA and EDDS addition levels. The highest dry matter reduction was obtained from leaves and stem parts of the plant with 1.0 mmol/kg for DTPA and 7.5 mmol/kg for EDDS for both the 10 and 15 mg/kg Se contamination level in the soil (Figure 1).
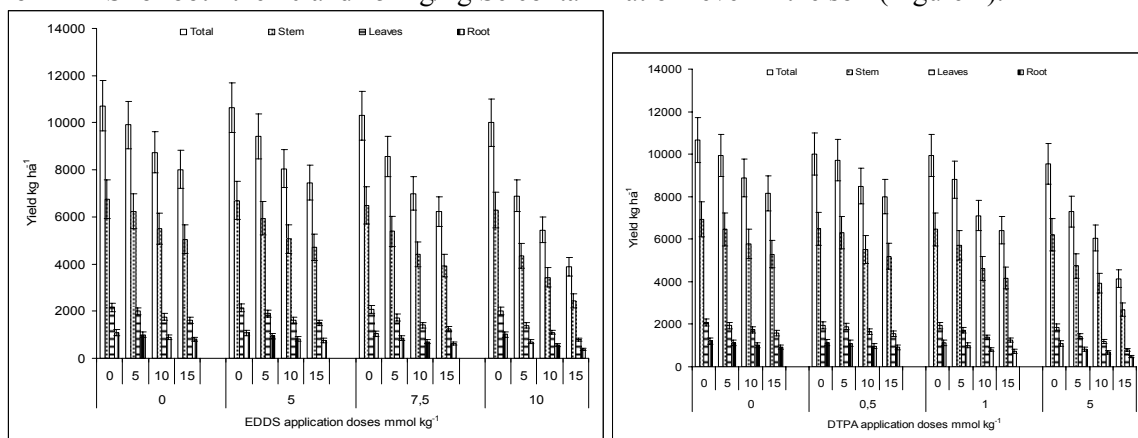


**Figure 1. Effects of DTPA and EDDS synthetic chelants on dry matter weight of different plant parts of Brussels sprouts grown on soil with different Se contamination**

*Efficiency of Synthetic Chelants Agents in Enhancing Soil Se Desorption:* All Se pools increased linearly with Se application with regression $R^2$ values of 0.90 or greater. Effects of synthetic chelants application significantly increased Se availability in soils. Se concentration in the soil increased with increased levels of DTPA and EDDS added to *Brussels sprouts* planted soils. The greatest increases with DTPA (5 mmol/kg) and EDDS (10 mmol/kg) addition at 15 mg/kg Se contaminated soil occurred in the most plant available fractions (water soluble and exchangeable), and followed the order of carbonate, metal oxide, organic matter bound and silicate bound fraction. Among the synthetic chelants tested, there were significant differences in their ability to stimulate total Se accumulation. Similar results were reported by Yadav *et al.* (2007), Sager and Hoesch (2006), Lu *et al.* (2006b), Wu *et al.* (2007).

*Heavy Metal Concentration in Leaves, Stems and Roots:* At all DTPA and EDDS application rates, Se concentrations in leaves were about 2-3 times higher than in roots and about 3-4 times higher than in stems (Figure 2). Although, leaves have the highest Se concentration, stem is more important portion of the plant to removal Se from the Se contaminated soil because of the fact that consist the biggest part of the plant. Application of DTPA and EDDS over 0.5 and 7.5 mmol/kg doses significantly decreased total Se uptake in leaves, stems and roots in plants (Figure 3). Similar increases in crop removal were reported by Ducsay and Lozek (2006), Srivastava *et al.* (2005), Yadav *et al.* (2007), Zhang *et al.* (2007), Li *et al.* (2008).
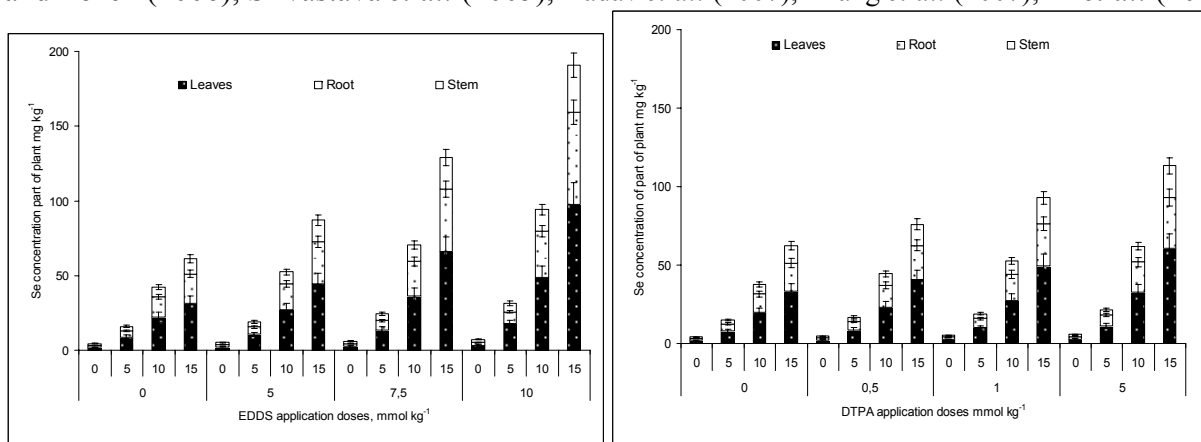


**Figure 2. Effects of DTPA and EDDS synthetic chelants on Se concentration in different plant parts of the Brussels sprouts grown on soil with different Se contamination**
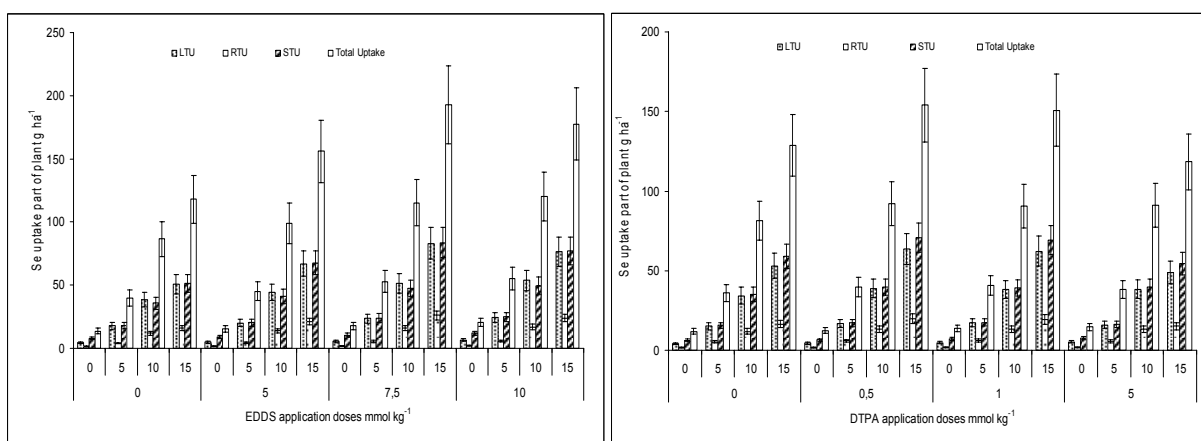


**Figure 3. Effects of DTPA and EDDS synthetic chelants on Se uptake by different plant parts of the Brussels sprouts grown on soil with different Se contamination**

## Conclusion

Phytoremediation is widely considered as low cost and ecologically-responsible alternative to the expensive physical-chemical methods currently practiced, and an emerging bio-based and low cost alternative technology in the clean-up of contaminated soils. The ability of DTPA and EDDS to release Se in soils planted with *Brussels sprouts* followed the order of EDDS>DTPA, respectively. Among the synthetic chelants tested, EDDS was the most effective for *Brussels sprouts*. The results of this study demonstrated that EDDS is an efficient soil amendment in enhancing Se desorption

from soil and for increasing Se accumulation in plants. More importantly, this chelating agent not only facilities heavy metal removal from the soil via plant uptake, but in theory means that any metal that can be chelated and solubilized can be removed in the same manner, providing the soil chemistry favors the forming of a chelate- metal complex.

**References**

AOAC (Association of Official Analytical Chemists-International) (2005) Official Methods of Analysis, 18th Edn. (Eds W Hortwitz and GW Latimer.), AOAC-Int. Gaithersburg, MD, USA.

Ducsay L, Lozek O (2006) Effects of selenium foliar application on its content in winter wheat grain. *Plant and Soil Environment* **52**, 78-82.

Huang JW, Chen J, Berti WR, Cunnigham SD (1997) Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction. *Environ. Sci. Technol.* **31**, 800-805.

Kos B, Lesˇtan D (2003a) Influence of a biodegradable ([S, S]-EDDS) and non-degradable (EDTA) chelate and hydrogel modified soil water sorption capacity on Pb phytoextraction and leaching. *Plant and Soil* **253**, 403-411.

Kos B, Lesˇtan D (2003b) Induced phytoextraction/soil washing of lead using biodegradable chelate and permeable barriers. *Environmental Science and Technology* **37**, 624-629.

Li H, McGrath SP, Zhao F (2008) Selenium uptake, translocation and speciation in wheat supplied with selenate or selenite. *New Phytologist* **178**, 92-102.

Luo C, Shen Z, Li X, Baker AJM (2006a) Enhanced phytoextraction of Pb and other metals from artificially contaminated soils through the combined application of EDTA-EDDS. *Chemos.* **63**, 1773-1784.

Luo C, Shen Z, Lou L, Li X (2006) EDDS and EDTA-enhanced phytoextraction of metals from artifically contaminated soil and residual of chelant compounds. *Envriional Pollution* **144**, 862-871.

McEldowney S, Hardman DJ, Waite S (1993). Treatment Technologies. In 'Pollution Ecology and Biotreatment'. (Eds S McEldowney, DJ Hardman, S Waite) (Longman Scientific & Technical, Singapore).

Mertens D (2005a) AOAC Official Method 922.02. Plants Preparation of Laboratuary Sample. Official Methods of Analysis, 18th edn. (Eds W Horwitz, GW Latimer) pp. 1-2., Chapter 3, AOAC-International Suite 500, 481. N F Avenue, Gaitherburg, (Maryland 20877-2417, USA).

Mertens D (2005b) AOAC Official Method 975.03. Metal in Plants and Pet Foods. Official Methods of Analysis, 18th edn. (Eds W Horwitz, GW Latimer). pp. 3-4., Chapter 3, AOAC-International Suite 500, 481. N F Avenue, Gaitherburg, (Maryland 20877-2417, USA).

McBride MS (1994) Environmental Chemistry of Soils. Oxford University Press, NY.

McGrath SP, Shen ZG, Zhao FJ (1997) Heavy metal uptake and chemical changes in the rhizosphere of *T caerulescens* and *T ochroleucum* grown in contaminated soils. *Plant and Soil* **188**, 153-159.

Sager M, Hoesch J (2006) Selenium uptake in cereals grown in lower Austria. *Journal Central European Agriculture* **7**, 71-78.

SPSS Inc (2004) SPSS Inc. SPSS® 13.0 Base User's Guide, Prentice Hall.

Srivastava M, Ma Q, Cotruva JA (2005) Uptake and distrubition of selenium in different fern species. *International Journal of Phytoremediation* **7**, 33-42.

Trapp S, Karlson U (2001) Aspect of phytoremediation of organic pollutants. *J. Soil Sedim.* **1**, 1-7.

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844– 851.

USDA and NRSC (United States Department of Agriculture and National Resources Conservation Service), (2000) Soil Quality Institute, Urban Technical Note No: 3, September 2000.

Vogeler I, Green SR, Clothier BE, Kirkham MB, Robinson BH (2001) Contaminant transport in the root zone. In 'Trace Elements in Soils: Bioavailability, Flux, and Transfer'. (Eds IK Iskandar, MB Kirkham) pp. 175-197. (Lewis, Publishers, Boca Raton, Florida).

Wu LH, Sun XF, Luo YM, Xing XR, Christie P (2007) Influence of (S-S)-EDDS on phytoextraction of copper and zinc by Elsholtzia Splendens from metal contaminated soil. *International Journal of Phytoextraction* **9**, 227-241.

Yadev S, Gupta S, Prakash R, Spallholz J, Prakas NT (2007) Selenium uptake by *Allium cepa* grown in Se-spiked soils. *American-Eurasian J. Agric and Environ. Sci.* **2**, 80-84.

# Transport and fate of contaminants in soils: challenges and developments

**Brent Clothier**[A], Steve Green[A], Markus Deurer[A], Euan Smith[B] and Brett Robinson[C]

[A]Production Footprints, Plant & Food Research, PB 11-600, Palmerston North, New Zealand 4442, Email brent.clothier@plantandfood.co.nz
[B]Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, Adelaide, Australia
[C]Department of Soil & Physical Sciences, Lincoln University, Canterbury, New Zealand

## Abstract

Human and environmental risk due to contaminants is quantified as the product of hazard and exposure. For many soil and water contaminants, such as heavy metals or organic compounds, the hazards are well known. The challenge is to determine better the exposure pathways. For emerging contaminants, such as nanoparticles, both the toxicity and exposure pathways are unknown. A pollutant's risk can be due either to the continued residency in the soil, or their subsequent fate in receiving waters. Transport of pollutants through soil defies robust prediction currently due to preferential flow processes along macroporous networks, and this is compounded by spatial heterogeneity in the sources of contamination. However, hard-won biophysical knowledge of chemicals moving through soil is increasingly being incorporated into decision support tools to guide risk assessment policies and to assist with risk-based prevention and remediation practices.

## Key Words

Risk assessment, modelling, preferential transport, point-source pollution, decision support tools.

## Introduction

Contaminants in our soils and waters can detrimentally impact on ecological health and human well being. To assess the risk of such deleterious outcomes, it is necessary to consider the hazard, or toxicity, of the contaminant, along with the likelihood of environmental or personal exposure to the pollutant. Risk is thus quantified as the product of hazard and exposure. For many soil and water-borne contaminants, such as heavy metals or organic compounds, the level toxicity or hazard has been quantified. The challenge is to quantify better the exposure pathways. For emerging contaminants, such as nanoparticles, little is yet known about hazard levels, and so risk assessment is doubly difficult for there needs to be better quantification of both toxicities and exposure pathways. In this presentation we focus, for both traditional and emerging contaminants, on the pathways of exposure which depend on the transport and fate of pollutants in the soil.

We highlight the challenges we currently face in developing the requisite knowledge to enable apt modelling frameworks to be developed for prediction the transport and fate of contaminants in soil. Nonetheless, we show how by using current understanding it is possible to develop decision support tools for risk assessments and for strategies of remediation based on minimising risks to people and the environment.

A prime exposure pathway, either directly or indirectly, for soil-borne contaminants is via transport in the pore-water solution though the structured and chemically reactive medium of our soils. Soils are also home to plant roots and a myriad of floral and faunal denizens. We highlight the issues around preferential flow, and discuss how the spatially heterogeneous nature of point sources of contamination can make modelling difficult. In predicting pollutant transport, we distinguish between whether the fate is in the soil itself, or in receiving waters. The active role of vegetation in controlling the hydraulic impetus for pollutant transport is highlighted, as is its potential role in risk-based prevention and remediation. Next, we present new results on the transport of nanoparticles through soil. Finally, we provide the results of our recent efforts to capture our measurements and modelling in a decision support tool to assess the health risk of consuming vegetables grown in heavy-metal contaminated soil.

## Preferential Flow

Soils are three-phase media, characterised by complex porous structures. New measurement technologies are resolving the impact of these structures on the transport and fate processes that control exposure to pollutants (Deurer *et al*. 2008; Gee *et al*. 2009). Increasingly these new measurements and monitoring devices are revealing the prevalence of water repellency and its linkage to transport processes from the soil

surface down to underlying groundwaters.

Hydrophobicity:  The surface, and some sub-surface, zones of many soils when they dry out below a critical water content exhibit water repellency such that they do not spontaneously absorb water during infiltration.  This can result in a free-water pond on the surface or zones of positive water potential heads deeper in the profile.  Free water can then access the macroporous networks, at least until hydrophobicity weakens (Figure 1).

Macroporous networks:  Once accessed, soil water and its entrained chemicals are provided a rapid and far-reaching ride past the otherwise reactive surfaces of soil's matrix.  This results in preferential transport towards receiving water bodies, with little adsorption or degradation of pollutants (Figure 1).
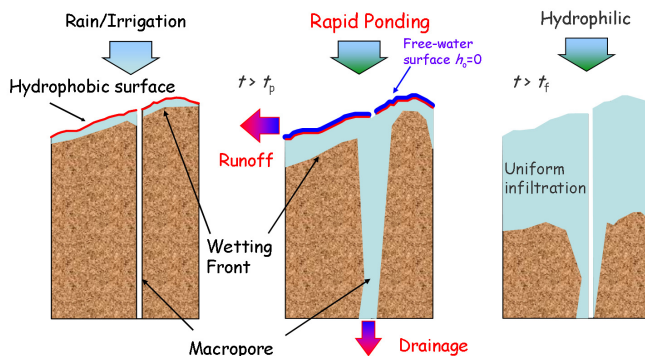


**Figure 1.  The temporal pattern of wetting and flow in a soil which exhibits transient water repellency (from Clothier *et al.* 2008).  During the hydrophobic stage (middle) there is a surface free-water surface that leads to runoff and macropore flow.  After repellency wanes (right) wetting occurs through the matrix, depending on the rainfall rate and the soil's conductivity.**

Filtering and Buffering - Exogenous and indigenous contaminants:  A common pattern of soil wetting and transport shown in Figure 1 has quite different ramifications for pollutant transport.  If the contaminant were exogenously incident on the soil surface, then in the middle panel of Figure 1 this would result in deeper-than-expected transport and fate of contaminants.  If the pollutant were already indigenous, say mineralised nitrogen, then greater transport would occur under the right-hand conditions of Figure 1.

**Point sources and spatial patterns**
Contaminants often do not land, or are applied, to soils in a uniform manner.  As we show in Figure 2, contaminants need not arrive on, or into the soil, in a homogeneous pattern. For treated posts containing copper, chromium and arsenic (CCA), their point sources of pollution demand special recognition of the spatial configuration of the leakage sources.  The dark green spots in Figure 2 are animal urine patches and a risk assessment of their likelihood of contaminating ground and surface waters requires that especial treatment be given to the nitrogen dynamics within those spots. Assuming uniformity leads to erroneous risk assessment.

**Fate: Soil or receiving waters?**
The assessment of risk needs to consider whether the exposure pathway is via contaminants that become adsorbed and resident in soil, or whether the exposure is through impact on receiving waters, which itself is dependent upon local hydrogeology.  These impacts are shown to be quite different, here in the case for CCA leakage from treated support posts in vineyards.  The impact of urine spots on groundwaters is also highlighted, and the errors resulting from assuming a uniform distribution is quantified.

**Vegetation: Controlling the upper boundary**
Soil is not only a reactive physico-chemical medium, it is also hosts plant roots and a teeming microbiological ecosystem. Biological processes, in particular the role of plants in controlling hydraulic processes and the hydrology of soil needs to be closely considered in predicting the fate and transport of contaminants in the rootzone.  Further, the biophysical and chemical uptake role of plants needs to be considered as a key part of risk-based assessments of the ability of phytomanagement to control and limit the impacts of soil-resident pollutants.

**Figure 2. When assessing the risk of contamination from point sources, such as CCA leakage from fence posts, or nitrate loss from urine spots in pastures, it is necessary to account for the spatial pattern in the landscape of the point sources of contamination.**

### Nanoparticles

Modern engineering processes have provided a welter of very small-sized particles that are used in a wide range of appliances, cosmetics and devices. These so called nanoparticles are tiny (Figure 3), and their surface area to size ratio is huge such that they could be implicated in disrupting metabolic processes in nature and for humans. Not only is little known about the human health and environmental hazards they pose, there is a dearth of understanding of how they move through soil-plant-faunal systems.

We describe here some preliminary experiments on measuring the transport of fluorescent quantum dots through soils. Such measurements are first needed to provide the knowledge that will be required to develop modelling frameworks for predicting exposures.
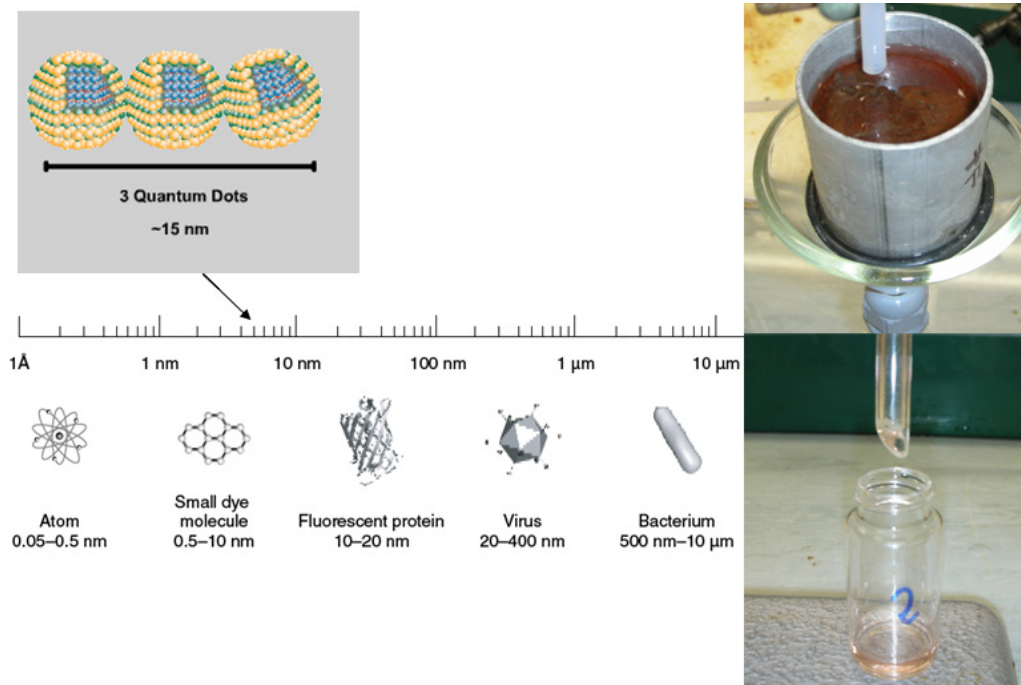


**Figure 3. Left. Quantum dots, which fluoresce, comprise a shell and core of different elements. They are very small in relation to other compounds that are likely to be found in soils and plants. Right. One of our simple breakthrough experiments with steady flow through a saturated soil core. Nanoparticles of fluorescent quantum dots of cadmium-tellurium were applied as a pulse in a solution to the soil surface (top) and aliquots of effluent solution (bottom) were then analysed for quantum dots and the conservative bromide tracer.**

**Decision support tools**
Measurements using new devices and novel techniques are shown to be providing confidence for the modelling that is required to develop decision support tools that can be used to guide risk management policies and develop risk-based remedial actions. We demonstrate this for exposure to heavy metals through the consumption of vegetable grown in contaminated soils.

**Conclusions**
For known contaminants, the challenge is to better understand how risk depends on the exposure pathways resulting from transport and fate processes in the soil. For emerging contaminants, this exigency is heightened by the need to understand better their hazards.

**References**
Clothier BE, Green SR and Deurer M (2008) Preferential flow and transport in soil: Progress and Prognosis. *European Journal of Soil Science* **59**, 2-13.

Deurer M, Clothier BE, Green SR, Gee G (2008) Infiltration rate, hydraulic conductivity and preferential flow. In 'Soil Science: Step-by-step Field Analyses' (Eds. SD Logsdon *et al.*), pp. 221-233. Soil Science Society of America.

Gee GW, Newman BD, Green SR, Meissner R, Rupp H, Zhang ZF, Keller JM, Waugh WJ, van der Velde M, Salazar J (2009) Passive-wick fluxmeters: Design consideration and field applications Water Resources Research DOI 10.1029/2008WR007088.

# Use of monitored natural attenuation in management of risk form petroleum hydrocarbons to human and environmental receptors

Peter Beck[A]

[A]GHD Pty. Ltd. Melbourne Australia Level 8, 180 Lonsdale Street, Melbourne.

**Abstract**
Monitored Natural Attenuation has potential for passive remediation of dissolved phase petroleum hydrocarbon impacts in groundwater. The successful application to any groundwater contamination situation is dependent on a number of factors. Soil conditions affect both the physical and chemical aspects of natural attenuation processes. Key soil related aspects include retention of hydrocarbon mass, groundwater flow regime and hydrocarbon degradation rate. Risk is another element that needs to be considered, particularly in relation to volatile vapours that could affect human health. Therefore the risk aspects, both present and future need to be understood. Finally the nature and character of the source is a critical aspect that establishes whether monitored natural attenuation can be utilised to manage or remediate dissolved phase hydrocarbons in groundwater. While from a technical standpoint monitored natural attenuation would revolve around the collection of primary, secondary and tertiary lines of evidence to demonstrate natural attenuation is occurring, soil properties, risk and source aspects also need to be considered in decision making.

**Introduction**
Monitored natural attenuation (MNA) has been utilised for passive remediation of petroleum hydrocarbon impacted soil and groundwater for over two decades. Most application has occurred in situations where primary and secondary source zones have been remediated and natural attenuation was used to deal with the residual soil and groundwater impacts. Over the last decade a number of guidance documents have been developed to guide the process and demonstrate the applicability of MNA (Sinke and le Hencho, 1999; WSDE, 2005), including the recent guidance prepared by CRC CARE on the technical aspects of implementing MNA strategies.
Technical consideration for implementation of MNA projects for Petroleum Hydrocarbons (TPH, BTEX, PAH) include their properties and behaviour in the environment, as well as natural attenuation processes (ASTM, 1998; Blum *et al.* 2007; McAllister *et al.* 1994). Following consideration of the contaminants and the environment in which they occur, collection and interpretation of the primary, secondary and tertiary lines of evidence are required to demonstrate that natural attenuation is capable of limiting the spread of hydrocarbons to within an acceptable extent (DEP, 2004; EA, 2000). Limitations and uncertainties associated with implementation of an MNA project include affects of primary, secondary and tertiary source activity and presence of Light Non-Aqueous Phase Liquid (LNAPL) with associated effects on MNA performance (Rice and McNab, 199; Chapelle *et al.* 2003; Wiedemeier *et al.* 1995; Wiedemeier and Haas, 1999). Effects of heterogeneous and dynamic geological, hydrogeological and hydrogeochemical conditions also need to be considered. This paper focuses on two technical aspects of implementing an MNA strategy that are often not directly considered in the technical evaluation of the approach.

**Importance of Soil Condition**
Soil conditions can have a critical influence on the performance of and the duration over which an MNA strategy needs to be implemented (Chapelle *et al.* 2003; Wiedemeier *et al.* 1995). Implementing MNA in homogenous isotropic soils results in limited uncertainty in regards to performance. When dealing with heterogeneous anisotropic conditions however, the uncertainty can be significant and may result in stakeholders being reluctant to accept MNA (USEPA, 1994; WSDE, 2005). The key areas where soil conditions can have a significant effect on the performance of MNA are:
– Retention of residual trapped free phase hydrocarbons that act as a long term source. This trapped phase usually occurs as discrete globules of product within the soil pore space. As a consequence a high surface area is available for the dissolution of the hydrocarbons into the groundwater leading to increased mass loading and longer plumes. Therefore understanding the thickness of the residual phase is important when estimating timeframes for remediation, mass loading characteristics and the size and scale of the plume that may develop;
– Groundwater flow is strongly influenced by the properties of the soil. The nature and interconnectivity between pore spaces through which groundwater travels have a fundamental influence on the velocity of

flow as well as the dispersion of the contaminant (Figure 2). Differences in flow velocity result in differential travel within portions of the plume causing differential concentration distribution due to advection. Dispersion is also affected and generally assists in biodegradation as many constituents in petroleum products become less toxic as concentrations decrease, allowing biodegradation to occur; and

–  Degradation of hydrocarbons occurs through oxidation – reduction reactions that are facilitated by micro-organisms. These organisms live in biofilms on the surface of soil grains and their survival is dependent on the presence of carbon and nutrients that facilitate the biological cycle. Therefore variability in the presence of these within the soil matrix causes differential rates of biodegradation;
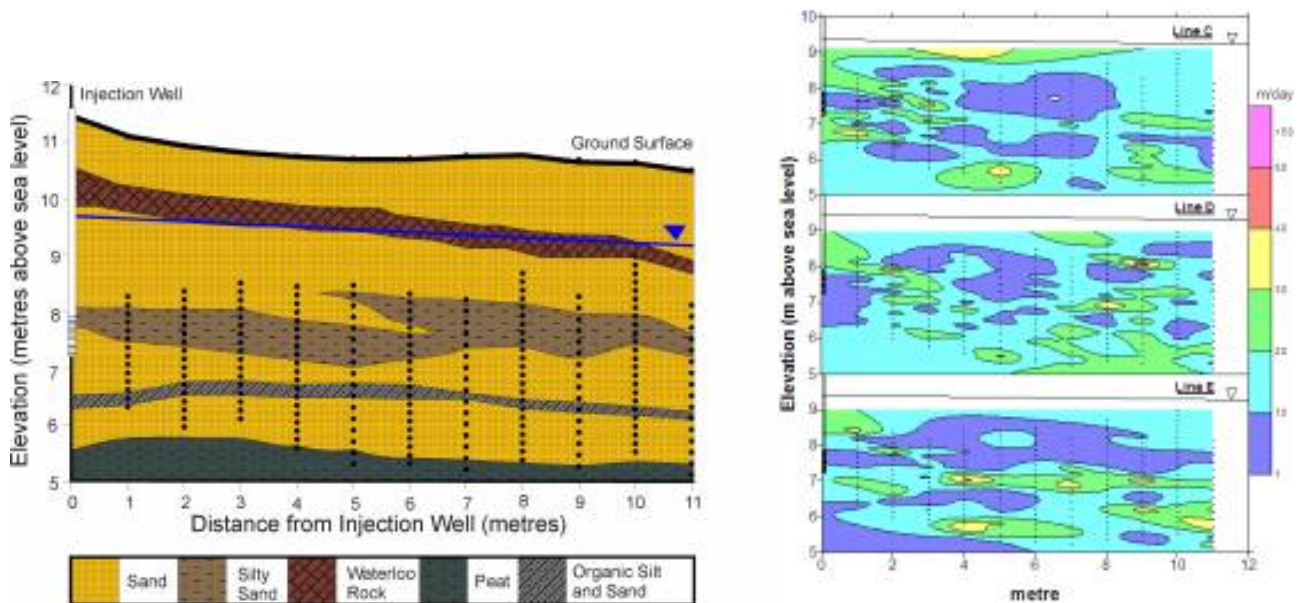
–



**Figure 2. Effect of small heterogeneity on hydraulic conductivity in the Botany Sand Aquifer (Beck and Jankoski 1998).**

These soil related aspects can often affect the performance of MNA strategies but are not commonly included in site characterisation investigations which focus largely on groundwater sample analysis and plume delineation. In most situations they may not need to be extensively considered in the initial stages of MNA if progress is anticipated but may require consideration, should there be unanticipated performance characteristics.

**Understanding Risk**
Another aspect often not included in the early stages of assessment for MNA viability is consideration of risk from volatile emissions by free, residual and dissolved phase product, particularly in relation to land use or land use changes in the area overlying the plume. The risk is often highly dependent on the nature of the soils that overlie the impacted zone and hence have a significant influence on the risk posed.
Understanding the potential risk due to vapour migration into buildings overlying the plume is an important pre-requisite when considering implementation of a MNA strategy to deal with dissolved phase hydrocarbon impacts, particularly considering that the timeframe involved may be extensive. Therefore considering the risk in terms of the conceptual site model such as the example shown on Figure 3 is important to the development of a clear understanding of the applicability and uncertainty associated with any MNA strategy.

**Management versus Remediation using MNA**
A third element that must be considered in any MNA strategy is whether the objective is to remediate the impacts or manage them until remediation can be undertaken. Groundwater impact by dissolved phase hydrocarbons occurs as a consequence of mass loading from primary (fuel storage and dispensing infrastructure) and secondary sources (impacted soils with free and sorbed phase hydrocarbon impact). The presence of free phase LNAPL further complicates the source and mass loading mechanism. In most situations removal of primary and most of the secondary sources is practicable. However, the presence of LNAPL on the water table and the associated formation of a smeared zone with trapped hydrocarbons in the soil pore space due to hydraulic head fluctuations is more difficult to remediate, particularly if they occur at depth (USEPA, 1994; USEPA, 1997; USDN, 1998). Therefore an ongoing source remains and is subject to degradation over time. The rate of degradation of the source is highly dependent on the environment and can

lead to long-term (decades) mass loading of dissolved phase to the groundwater (Chapelle *et al.* 2003; Wiedemeier *et al.* 1995; Wiedemeier and Haas, 1999).
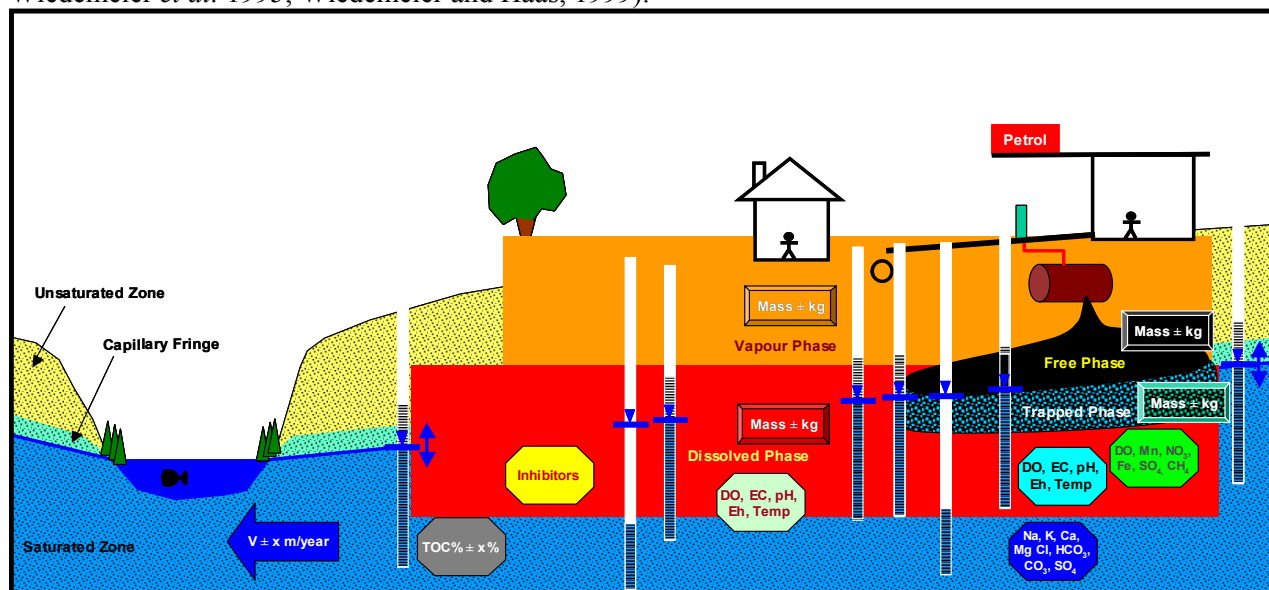


**Figure 3. Example of a conceptual site model that includes consideration of the source, pathway and receptor linkage (CRC CARE unpublished draft).**

Clearly in situations where an ongoing long term source remains, implementation of an MNA strategy would lead to the requirement for monitoring over an extended period and clean up would only be achieved once the source mass loading ceased (WSDE, 2005). Clearly these extended timeframes to reach clean up may not be acceptable to some stakeholders and therefore more active remediation may be required. However complete removal of all sources may not be practicable, for example at facilities with ongoing hydrocarbon storage and dispensing infrastructure in source zones limiting access. In these situations, MNA may be used to manage the resultant dissolved phase plume until such time when remediation can be accomplished. Therefore MNA may be applied as either a remediation technology if the timeframe to meet clean up goals are acceptable to stakeholders or alternatively if long timeframes are required or source clean up is not pragmatic then MNA may be used as a management strategy until more active clean up becomes feasible.

**Conclusion**
Therefore MNA is a strategy that can be applied to remediation or management of dissolved phase hydrocarbons. While the technical aspects and lines of evidence for demonstrating the occurrence of natural attenuation processes are extensively documented, there are a number of important considerations that can affect the applicability, effectiveness and duration of an MNA strategy.  Soil properties affect retention of residual phase, groundwater flow and biodegradation, while the volatility affects risk that may limit the applicability of an MNA strategy. The character of the source also affects the duration over which an MNA strategy needs to be applied.  CRC CARE identified the need to develop a nationally consistent approach to the implementation of MNA strategies that outlines the key technical requirements to demonstrate MNA as well as note factors that affect the applicability, efficiency and duration of MNA strategies, such as those outlined in this paper. In response a national technical guidance document on implementation of MNA strategies was developed, incorporating technical requirements, as well as aspects that result in limitations and uncertainties and minimum data requirements.

**References**

American Society for Testing Materials (ASTM) (1998) Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites. E 1943 – 98, ASTM International, West Conshohocken.

Beck PH and Jankowski J (1998), A small scale dispersion experiment in a heterogeneous sandy aquifer, Botany Sands aquifer, Sydney, Australia, International Groundwater Conference, Groundwater Sustainable Solutions, The University of Melbourne, 8-13 February 1998, Melbourne, Australia.

Blum P, Hunkeler D, Weede M, Beyer C, Grathwohl P, Morasch B (2007) Quantification of biodegradation

for various organic compounds using first-order, Michaelis-Menten kinetics and stable carbon isotopes, Geophysical Research, Vol. 9, 07285

Chapelle FH Widdowson MA Brauner JS Mendez III E and Casey CC (2003) Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation. Report 03-4057, USGS, Columbia.

Department of Environmental Protection (DEP) (2004) Use of Monitored Natural Attenuation for Groundwater Remediation, Land and Water Quality Branch, Environmental Regulation Division, Department of Environmental Protection, Perth.

Environment Agency (EA) (2000) Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater. R&D Publication 95, Environment Agency, Bristol.

McAllister PM, Chiang CY (1994) A practical approach to evaluating natural attenuation of contaminants in groundwater. *Groundwater Monitoring Review* (Spring 1994) 161-173.

Rice DW, McNab WW (1998) Natural Biodegradation of Organic Contaminants in Groundwater. Lawrence Livermore National Laboratory, UCRL-JC-131848.

Sinke A, le Hencho I (1999) Monitored Natural Attenuation: review of existing guidelines and protocols. 2864, TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Apledoorn.

US EPA (1994) Symposium on Natural Attenuation of Groundwater. EPA/600/R-94/162.

US EPA (1997) Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17.

US Department of the Navy (USDN) (1998) Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities.

Washington State Department of Ecology (WSDE) (2005) Guidance on Remediation of Petroleum-Contaminated Ground Water By Natural Attenuation. Publication No. 05-09-091 (Version 1.0), Washington State Department of Ecology, Olympia.

Wiedemeier TH, Wilson JT, Kampbell DH, Miller RN, Hansen JE (1995) Technical Protocol for Implementing Intrinsic Remediation with Long Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, Air Force Centre for Environmental Excellence.

Wiedemeier TH, Haas P (1999) Designing Monitoring Programs to Evaluate the Performance of Natural Attenuation. In 'Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds 5(1)', pp. 313-323. (Battelle).

# Use of some methods for risk assessment of arsenic load in soils

Radim Vacha[A], Hana Macurova[A], Jarmila Cechmankova[A], Hana Javurkova[A] and Jan Skala[A]

[A]Research Institute for Soil and Water Conservation, Zabovreska 250, Prague 5, 156 27, Czech Republic, Email vacha@vumop.cz

## Abstract

The contribution deals with the methods of arsenic analysis for soil. The selection and verification of the methods for As analysis which seem to be suitable for risk evaluation following from increased As soil load is presented. Economical and analytical availability of the methods is an important criterion. A sample set of 6 heavily contaminated soils was used to compare testing methods. The results showed that substitution of analytically more demanding As total content analysis and sequential analyse using simple extraction with one-off agents is promising in many cases. The comparison and evaluation of statistical correlation of used methods of As analyse in the soil was realised. The results confirmed that the use of the combination of simple 1M $NH_4NO_3$ extraction and determination procedure for amorphous Fe forms in the soil (the Tamm method) was suitable for the definition of main risks, following from As contamination without necessity of application of more complicated sequential extraction procedures.

## Key Words

Arsenic, agricultural soils, soil contamination, chemical methods, load evaluation, methodical approach.

## Introduction

Arsenic belongs to the group of trace elements and an increase in soil load of As may lead to many environmental risks, including As toxicity for living organisms. An increased As concentration in human organism can cause carcinogenic and teratogenic symptoms. Abedin *et al.* (2002), Yerebakan *et al.* (2002) document and discuss it more detailed. Arsenic can be usually found in inorganic forms – arsenite [As(III)] and arsenate [As(V)] in the soil. As generally occurs in the pentavalent state in the soil because the As (III) form oxidizes to the As (V) form. The pentavalent form of As is less toxic. Although As human and zootoxicity is reported, many authors deal with how As influences plant growth and plant physiology (Das *et al.* 2008). Increased soil As can be caused by geogenic and anthropogenic sources. Primarily atmospheric deposition, floods and load spreading round mine dumps leads to the anthropogenic As contamination of the soil (Vácha *et al.* 2002). In the soils of the emission– free regions there particularly prevails As content of geogenic origin. According to the As present in rocks there can be distinguished two categories of geogenic load - lithogenic and chalcogenic. Both types of As geogenic load occur in the Czech republic. Solving the question of the ratio of geogenic and anthropogenic loads rests on the assessment of the spatial distribution of the soil substrates indicating geogenic soil load (Němeček *et al.* 1996; Vácha *et al.* 2002). Different As bonds significantly influence plant uptake of As.

Sequential extraction procedures (SEPs) have been developed to assess limits of element contents in plants. Comparing the extractability of As, Cd, Zn in 35 soil samples with different physiochemical properties, Száková *et al.* (2001) found that As and Zn contents extracted in low strength reagents have not exceeded 0.5% of their total contents in soils. Among used extraction agents the 0.01M $CaCl_2$ solution seems to be the most appropriate for the extraction of elements (Száková *et al.* 2001). Extractions in 1M $NH_4NO_3$ and 0.025M EDTA (ethylenedinitrilotetraacetic acid) are used predicting mobile or potentially mobilizable contents of risky elements in the soil (Podlešáková *et al.* 2001). The methods of sequential analysis can be used for detailed studies of different As forms in the soil. The Zeien and Brűmer (1989) SEP procedure is used for potentially risky element assessment in the Research Institute for Soil and Water Conservation (RISWC).

The application of this method for soil As with its the anionic nature can be disputed. Therefore specific schemes and sequential analyses for the assessment of soil As have been developed (Wenzel *et al.* 2001). Because of the growing number of analytical methods their comparability is problematic and a European recommended standard for SEP for some risky elements (BCR EUR 19775 EN) has been developed. This procedure was tested for our soil conditions in the study carried out by Száková *et al.* (1999) –set on a of 35 Czech soils. It was found that there is a large proportion of residual immobile As fraction bound to silicates (75%) in monitored soil samples. The results of this SEP were compared with the results of two another

analytical schemes and was ascertained that the extractable As ratio was different and hardly comparable for different methods. Nevertheless a statistically significant correlation of analytical data suggested that trends in the As distribution into main soil fractions was reflected by the applied extraction scheme.

**Material and methods**
Six soil samples were used with increased As contents with different sources of As (emission out-puts, fluvial load, geogenic load). Only humic horizons of agricultural soils were used for the sampling. Soil properties were analysed in the Research Institute for Soil and Water Conservation in Prague. The grain size distribution (5 categories) used burette method. Soil pH in the extract of 1M KCl and the value of cation exchange capacity (mmol+/100g) were measured for soil samples. Soil organic matter ($C_{ox}$) water-soluble carbon ($C_{ws}$), hot water-soluble carbon ($C_{hws}$) and organic carbon ($C_{ox}$) were measured. The quantity of humus (the carbon content of humic and fulvo acids measured in a solution of sodium pyrophosphate) and quality of humus (the ration of the carbon in humic and fulvo acids) was analysed. The total content of As was extracted with the acid mixture ($HNO_3$ + $HClO_4$ + HF) and was also the content extracted with 2M $HNO_3$ under cold conditions was analysed by AAS (Varian 240).  Besides the total Fe content there were determined Fe species in soil samples to elucidate an interaction between the As and Fe content. The Fe content extracted with pyrophosphate, ammonium oxalate and dithionate were measured (Burman *et al.* 1996). The crystalline Fe form and the ratio between Fe bound into amorphous and crystalline oxides and the Fe compared with organic matter (the chelate bond) were calculated from the difference of Fe content in ammonium oxalate and dithionate extracts.

The As contents in the characterised soil fractions were analysed using of three sequential extract procedures (SEPs). The first one is the method by Wenzel *et al.* (2001) that was developed for soil As especially by the modification of the Zeien and Brümmer (1989) SEP. The second technique in use was the fractionation in accordance to the BCR 701 EUR 19 775 EN (2001) norm relevant for number of risky elements in diverse materials (sewage sludge, soil). The third method was the scheme according to Zeien and Brümmer (1989). Our survey attempted not only to test individual methods but also to look for the possibilities of using simpler, economically and analytically less demanding methods while maintaining comparable predicative ability to sequential schemes. By the use of SEPs there is commonly 20% measurement uncertainty for the As assessment in individual extracts. If the uncertainty value reaches 20 % in the first step of the Zeien, Brümmer SEP, then it increases up to c. 53% in the seventh step. The SEP for the simultaneous extraction could thus be replaced using several one-off extraction agents. Considering the chemical similarity of P and As and the assumption that both elements are particularly associated with hydrated Al, Fe oxides, one-off extraction agents can be then divided into 2 categories. The first class includes soft agents that are used for the assessment of mobile and potentially mobilizable portions of risky elements (Száková *et al.* 2001). In regard of gathered experiences we prefer using 1M $NH_4NO_3$ (for mobile contents) and 0.025M $Na_2EDTA$ for potentially mobilizable contents. Especially the first scheme is crucial if only for the reason that it is employed as the international standard for the soil quality evaluation (ISO/DIS19730).

The established As association with the soil Fe oxides provides an opportunity for evaluating the procedure for the assessment of Fe and Al active forms significant for P fixation in the soil. The Fe-associated As content is then compared with the contents of other soil As forms of interest. For those purposes we used the extraction procedure originated by Tamm (1922) intended for the determination of amorphous Fe forms and based on extraction using ammonium oxalate and oxalic acid. This scheme was successively modified with respect to instrumental technique progression (Buurman 1996). All measurements have been carried out twice in three repetitions. The summary results of measurements have been processed by elementary statistics. Correlation analysis using ANOVA method and the Pearson correlation coefficient calculation have been accomplished.

**Results**
There were basic differences in the quantification of As content in defined soil fractions during the SEP testing for the assessment of As in the set of samples with the different type and level of contamination. The Wenzel procedure and the Zeinen and Brűmer technique proved the dominant As association with amorphous and crystalline Fe and Al oxides in the soils. The proportion of amorphous to crystalline oxides is mainly given by the soil matrix and by the load type. There was a characteristic a balanced ratio with a moderate dominance of the As association with crystalline Fe oxides (due to the primary As incorporation into the crystal lattice of the minerals) for soil samples with the geogenic load. The ratio was most likely

dependent upon the stage of the soil matrix weathering and upon the process of anthropogenic input of As into the soil (emission fallout, flood). Using the BCR technique there was detected a major ratio of As in the residual fraction most likely caused by the analytical scheme in the second extraction step (targeted on the As bound into Mn, Fe oxides).

This extraction step is not sufficiently selective to As detection. The detection of Mn, Fe associated arsenic is during the determination of the residual As fraction using the aqua-regia extraction. There may be a dominant arsenic portion in the residual fraction using the method by Száková *et al.* (1999) as well. With the BCR technique the organically associated As fraction amounted to low level values and did not exceed the Wenzel proportion values of the organically bound As to other soil fractions (2 – 7%). There was achieved a preferable correlation between the 2M $HNO_3$ extraction and easily exchangeable soil As using the Wenzel and the Zeinen and Brűmmer procedures. The BCR method was less sensitive to the exchangeable soil As fraction. The BCR technique is not to be recommended for the assessment of As soil fractions. A high level correlation of differences in the As distribution to particular fractions (especially for As bound into Al, Fe amorphous oxides where Pearson correlation coefficient attained 0.908) was reached through using of the Wenzel and Zeien and Brűmmer SEP.

This ratio was quantitatively higher by 10% using the Wenzel technique. We are not generally inclined to the opinion that the content of As in individual fractions resulting from the application of the procedure are not utilisable. The Wenzel procedure can be preferred for more precise quantification owing to the probability of the lower analytical error alone. Within the testing of simple extraction procedures using soft extraction agents there is an assessment of the mobile As fraction in the 1M $NH_4NO_3$ extract used in the first extraction step of the Zeien and Brümmer SEP compared to the $NH_4NO_3$ extraction according to the international standard ISO/DIS 19730. The schemes differ in extraction duration as well as in the proportion of the extraction agent to the sample. Hence different absolute values of the As content (mg/kg) in both extracts can be expected. There can be assumed an ideal equilibrium stabilising between the sample and the extraction agent owing to the 24 h extraction interval, the final concentration is then c. 20 times the value resulting from the standard method ISO/DIS 19730. Nevertheless there was found very tight correlation (the Pearson correlation coefficient = 0.999) among results of As assessment in the 1M $NH_4NO_3$ extract using the procedures of interest.

The application of the simpler scheme by ISO/DIS 19730 can be considered in terms of simplicity and economy. Using 1M $NH_4NO_3$ refers to the assessment of the soil As mobile forms that are determining in terms of risks under consideration. A completely new approach to the As assessment is using the determination procedure for amorphous Fe in the soil (the Tamm method). The As content resulting from the Tamm method significantly correlates with the content of As associated with Fe and Al amorphous oxides analysed by SEPs. There results a statistically significant correlation among tracked parameters from the mentioned results. It is presumed that the Tamm method is suitable for the quick assessment the portion of As associated with amorphous Fe, Al oxides in the soil. This assessment approximates the total As content in the soil owing to the predominant proportional representation of soil As binding to mentioned fractions. This assumption will not be valid for organic soils with a minor mineral fraction (Wenzel *et al.* 2001). Obtaining required information on potential risk resulting from As load of the soil can be obtained by using of combination of simple 1M $NH_4NO_3$ extraction and the Tamm method (without the necessity of the application of more complicated SEPs).

**References**
Abedin MJ, Cootes-Howells J, Meharg AA (2002) Arsenic Uptake and Acumulation in rice (Oryza sativa L.) Irrigated with Contaminated Water. *Plant and Soils* **240**, 311-319.

Buurman P, Van Lagen B, Velthorst EJ (1996) 'Manual for Soil and Water Analysis'. (Backhuys Publishers: Leiden).

Das DK, Sur P, Das K (2008) Mobilisation of arsenic in soil and rice (*Oryza sativa* L.) plants affected by organic matter and zinc application in irrigation water contaminated with arsenic. *Plant, Soil, Environ.* **54**,

30 – 37.

ISO/DIS 19730 Soil quality – Extraction of trace elements using ammonium nitrate solution, International Organization for Standartization, 2006.

Němeček J, Podlešáková E, Vácha R (1996) Geochemical and anthropogenic soil load. *Rostlinná výroba* **42**, 535 - 541.

Podlešáková E, Němeček J, Vácha R (2001) Mobility and Bioavailability of trace elements in soils. In "Trace elements in Soil: Bioavailability, flux, and transfer". (Eds IK Iskandar, MB Kirkham) pp. 21-42. (Lewis Publishers: Boca Raton)

Száková J, Tlustoš P, Balík J, Pavlíková D, Balíková M (2001) A comparison of suitability of mild extraction procedures for determination of available portion of As, Cd, and Zn in soil. *Chemické listy* **95**, 179 - 183.

Száková J, Tlustoš P, Balík J, Pavlíková D, Vaněk V (1999) The sequential analytical procedure as a tool for fractionation of As, Cd and Zn mobility in soil. *Fresenius J. Analytical Chemistry* **363**, 594 - 595.

Tamm O (1922) Eine Metode zur Bestimmung der anorganischen Komponenten des Gelkomplexes im Böden. Mddr. *St.Skogsfor.* **19**, 387-404.

Vácha R, Němeček J, Podlešáková E (2002) Geochemical and anthropogenic soil loads by potentially risky elements. *Rostlinná výroba* **48**, 441 - 447.

Wenzel WW, Kirschbaumer N, Prohaska T, Stingeder G, Lombi E, Adriano DC (2001) Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* **436**, 309 - 323.

Yerebakan O, Ermis O, Yilmaz E (2002) Treatment of Arsenical Keratosis and Bowen's Disease with Acitretin. Int *J Dermatol* **41**, 84-87.

Zeien H, Brűmmer GW (1989) Chemische Extraktionen zur Bestimmung von Schwermetallbildungformen in *Bőden. Mitt. Dtsch. Bodenk. Gesell.* **59**, 505 - 510.

# Water balance and efficiency of landfill covers with layers of dredged material

Klaus Berger[A], Alexander Groengroeft[A] and Carsten Harms[B]

[A]Institute of Soil Science, University of Hamburg, Hamburg, Germany, Email k.berger@ifb.uni-hamburg.de, a.groengroeft@ifb.uni-hamburg.de
[B]Hamburg Port Authority (HPA), Hamburg, Germany, Email Carsten.Harms@hpa.hamburg.de

## Abstract
Since 1995/1996 the water balances and the long-term performance of a 4 m thick landfill cover system with a barrier of dewatered dredged material have been measured in-situ in a large-scale lysimeter (test field) on a landfill in Hamburg, Germany. The lysimeter is integrated in the landfill cover and was built in the same way to obtain representative measurement results. For more than 12 years until the end of data evaluation in November 2007, the whole cover system performed well. The average discharge below the barrier is 16 mm/yr and nearly constant all over the year with a slight seasonal pattern. Reasons for the good performance are the large thickness of the barrier, the large thickness and load of the layers above, the "slow" lateral drainage layer and the root barrier that smoothes the inflow into the drainage layer. The measurements will be continued.

## Key Words
Landfill cover systems, water flow, liner performance, liner leakage.

## Introduction
The operation of the port of Hamburg requires a continuous dredging of the river Elbe and the harbour basins. A part of the dredged material is contaminated with heavy metals and organic pollutants and has to be deposited in a landfill after being processed in a technical plant called METHA. The mineral barrier of the landfill cover system has been constructed with dredged material. Due to the inexperience of using dredged material in a cover and its the relatively unfavourable material properties (high organic content, high water content, high shrinkage potential) the water balance and the long-term efficiency of the landfill cover system have been investigated in a research project starting in 1995. The extensive measurement program of the research phase, carried out until 1999/2000 by the Institute of Soil Science, was largely reduced in the subsequent monitoring phase, carried out by HPA. About 12 years of measurement from 1995/1996 to November 2007 are now evaluated.

## Methods
*Layer design and construction of the test fields*
In 1995 two lysimeters (test fields) were constructed on the northern slope of the Francop landfill site, each 10 m wide and 50 m long in slope direction (inclination of 8 %). The "standard design field" FS has the standard cover design of the Francop site with the following layer sequence (Figure 1):
1. Vegetation of grasses and perennial weeds
2. 1.2 m top soil of loamy material, the uppermost 0.1 m being rich in humus
3. 0.3 m root barrier of compacted loamy material
4. 1.0 m lateral drainage layer of sand from dredged material
5. 1.5 m barrier of dredged material
6. a collection pan for the percolation water of the barrier

The construction of test fields was carried out by the same machinery, the same soils and the same quality assurance as the cover of the whole site in order to study cover systems with representative construction quality.

*Measurement program*
The measurement program comprises meteorological parameters (precipitation, air temperature, etc.), discharges from all layers (surface runoff, interflow on the root barrier, lateral drainage, discharge below the liner), soil hydrological data (matric potential with tensiometers, soil moisture with TDR), physical, chemical and mineralogical soil properties and water chemical properties (ions like $Cl^-$, $SO_4^{2-}$ etc.).
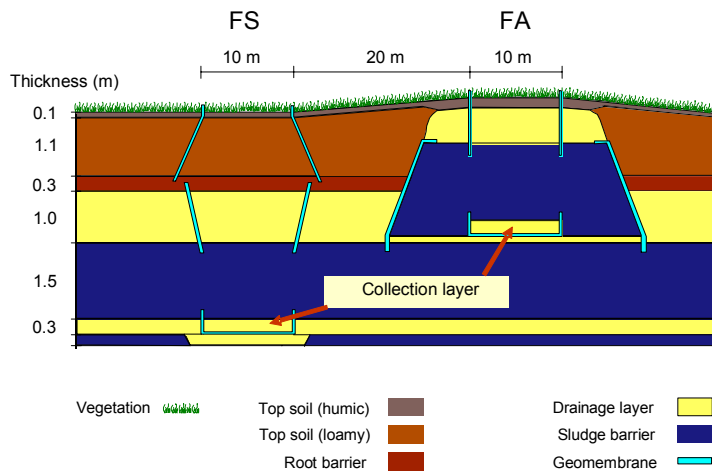
**Figure 1. Layer design of the test fields.**

## Results

The measurements on the standard design field FS from 1996 to 2007 led to the following main results (Figure 2):

- The annual surface runoff usually was very small (a few mm per year) except for the first year 1996 (28 mm) when the canopy of the vegetation was not yet closed and the years 2002 and 2007 when large amounts of the surface runoff were caused by particular extensive rainfalls.
- The average annual interflow on the root barrier was 28 mm/yr and had a relatively broad range of values (4 to 76 mm/yr). Like surface runoff also the discharge on the root barrier was largely related to particular extensive rainfall events.
- The annual discharge below the barrier was 16 mm/yr and relatively constant over the years. The daily discharge rates were nearly constant over the year. However, they show a slight seasonal pattern with maximum values in late summer and autumn and minimum values in late winter and spring which can be explained by temperature-dependent water movement.
- The largest annual discharge was lateral drainage. It largely depends on the inflow into the drainage layer which is mainly determined by precipitation and evapotranspiration. Other values (surface runoff, interflow on the root barrier, changes in water storage of the upper layers) are only of minor importance. The time series of the daily lateral drainage shows the pattern typical for drainage layers. Peaks of lateral drainage occurred as a reaction to large inflow / precipitation events followed by exponential decreases of the flow rates when the inflow into the drainage layer stopped.
- The time lags between the surface runoff, interflow on the root barrier and lateral drainage were relatively small and indicated that the discharges reacted almost immediately (often within a few hours) after a precipitation event.
- The water chemical analyses of the very mobile chloride ion ($Cl^-$) over time indicate that no fresh water has percolated the barrier until now. The percolation rate is so slow that still only pore water is discharged.

## Conclusions

The study allows the following conclusions:

- The barrier of processed dredged material has performed well for more than 12 years since construction. Though the material has a high risk of crack formation due to dewatering, no continuous cracks have occurred until now. This is likely caused by several reasons:
    1. the large thickness of the barrier (1.5 m in contrast to the minimum requirement of the German regulations for landfills of 0.5 m);
    2. the large thickness and the large load of 2.5 m sand and soil above the barrier;
    3. the "slow" lateral drainage layer on the barrier, which keeps its surface wet all over the year; and
    4. the root barrier on the lateral drainage layer, which probably smoothes the inflow into the drainage layer.
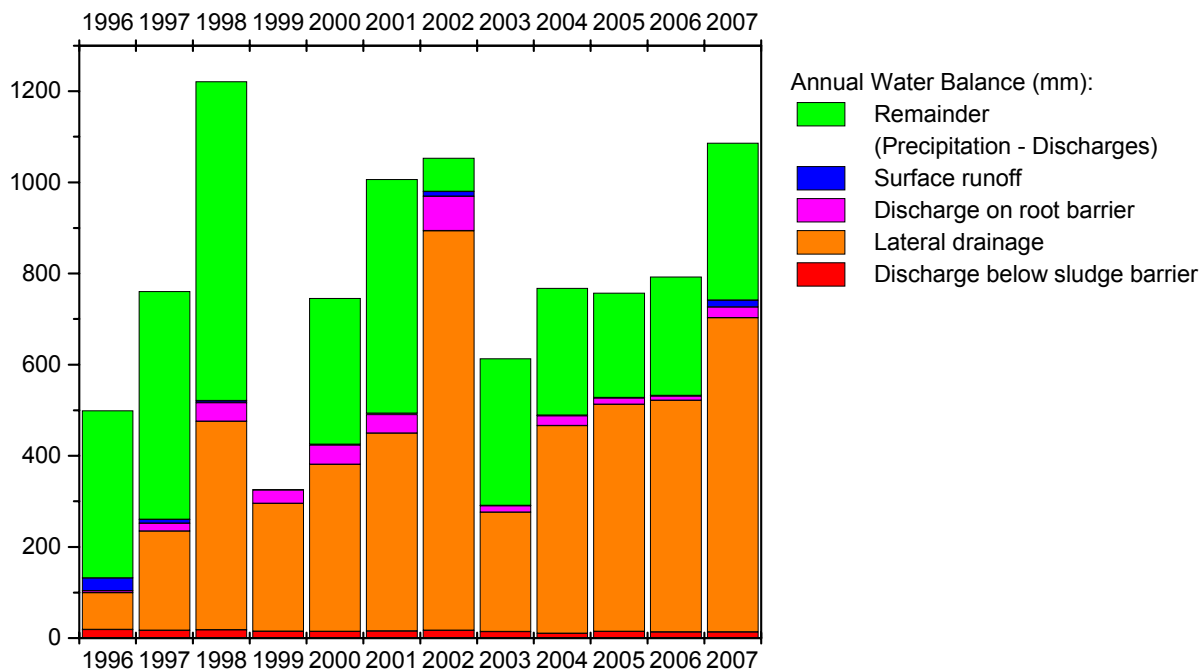
**Figure 2. Annual water balances (mm/yr) of test field FS (2007 incomplete: until 17.11.2007).**

- The lateral drainage layer made of medium sand has also performed well for more than 12 years. Its small saturated hydraulic conductivity ($0.7 \times 10^{-4}$ m/s, a factor of 14 smaller than the minimum requirement according to the German regulations) is compensated by a much higher thickness. Lateral drainage occurred all over the year. Therefore, it is reasonable to assume that the surface of the barrier was kept wet all over the year.

The whole 4 m thick cover system has performed well. However, due to the materials used and the slow biological, mechanical and hydrological processes the water balance and discharge measurements will be continued.

**References**

Blümel W, Tamminga PG (1987) Water permeability of dredged mud. In 'Proceedings of the Ninth European Conference on Soil Mechanics and Foundation Engineering'. (Eds. Hanrahan ET, Orr TLL, Widdis TF), pp. 545-548. (Balkema, Rotterdam).

Detzner HD, Schramm W, Döring U, Bode W (1998) New technology of mechanical treatment of dredged material from Hamburg harbour. In 'Proceedings of the International Conference on Contaminated Sediments'. (Eds W Calmano *et al.*), pp. 267-274. (Pergamon, Oxford).

Gröngröft A, Tresselt K, Harms C, Miehlich G (2001) Design and effectiveness of a landfill cover system based on sludge as barrier material. In 'Proceedings Sardinia 2001, Eighth International Waste Management and Landfill Symposium'. (Eds TH Christensen, R Cossu, R Stegmann) Vol III, pp. 317-324. (CISA: Cagliari).

Tresselt K (2000) Feldversuche zur Wirksamkeit von Oberflächendichtungssystemen mit Dichtungen aus Hafenschlick. PhD Thesis University of Hamburg, Germany. Hamburger Bodenkundliche Arbeiten 46, Hamburg. [Field tests on the efficiency of landfill cover systems with barriers of dredged material; in German].

# What is representative of the environment in the laboratory

Philip Mulvey[A] and Louise Cartwright[B]

[A]School of Earth and Geographical Sciences  University of Western Australia and Centre for Contaminant Geosciences, Unit 4, 2 George Place, Artarmon, Sydney, NSW Australia, Email pmulvey@eesi.biz
[B]Centre for Contaminant Geosciences, Unit 3, 1 Ross St, Newstead, QLD, Australia.

## Abstract
Successful bioremediation of soil at gas works sites is assessed by accurately collecting and analysing representative samples for total and leachable PAHs and comparing these with the risk derived site specific data using standard methods.  Analytical procedures are standardised to reduce error.  Unfortunately standardisation does not explore where the sub-sample is selected and whether the test chosen is representative.  Differences in laboratory sample selection, preparation, and extraction methods are so great that results can be meaningless even when standard methods are used.  This paper examines the various approaches adopted in regard to analysing total and leachable PAHs.  We found that results are being presented that are internally precise and accurate but are not representative.

## Key Words
Polycyclic aromatic hydrocarbons (PAHs), grinding, ultrasonic, soxhlet.

## Introduction
The aim of any investigation, remediation or validation is to deliver data that is: representative of what is sampled; precise; accurate; and reproducible.  A sample can be precise, reproducible and accurate but the question must still be asked as to whether it is representative of the environment.  This cannot be answered by the laboratory but only by the investigator.  The investigator must question whether a laboratory test represents what they are wishing to measure, as each test is designed for a specific purpose i.e. to measure a specific aspect of the soil environment (e.g. Curtis and Narayanan 1998).  This paper explores the ways in which current laboratory techniques and testing can vary between laboratories; how these variations influence data; and how individual PAH's physiochemical properties effect how a sample behaves under the differing preparation methods and extraction techniques.

## Error one: Random elevated concentrations (nugget effect)
The Enhanced Bioremediation process generally involves material to be screened, mixed and turned regularly (e.g. Van Deuren *et al*. 2002).  The mixing occurs several times and turning at least 15 times; this results in a relatively homogenised stockpile.  During the process the stockpiles are sampled at discrete time intervals for operational reasons.  It is common for stockpiles to exhibit a single random elevated organic compound (PAH) concentration approximately 1 to 3 months after the commencement of treatment.  Historically this single elevated result has been attributed to the 'nugget effect' which is considered to be spatial variability within the sample selected from the container, resulting in the sample not representing the remainder of the container (i.e. an imprecise result) (e.g. Starks 1986; Don Scott 2000).  The 'nugget effect' occurs as residual PAHs in the soil mass have been degraded and removed but PAHs in coke have not.  Therefore consistent results depend on creating a homogenous sample and not sampling areas that have a greater amount of coke in the sub sample than is generally found within the greater mass of the sample.  Data presented from a bioremediation project in Australia (Table 1) shows the variability of two (SR8-0.3m) and four (SP13-1) samples analysed from a single container.  This clearly shows that although the data presented by the laboratory is accurate and precise it is not representative of the stockpile or soil environment.

**Table 1. Replicates within a single Jar.**

|  | SP13-1 | SP13-1 Dup | SP13-1 Trip | SP13-1 Quad | SR8 -0.3m | SR8 -0.3m Dup |
|---|---|---|---|---|---|---|
| Phenanthrene | 18 | 1.2 | 1.1 | 1.4 | NT | NT |
| Anthracene | 8.6 | <1.0 | <1.0 | <1.0 | NT | NT |
| Pyrene | 15 | 2.3 | 2.5 | 3.4 | NT | NT |
| BaP | 11 | 1.3 | 1.9 | 2 | 100 | 0.23 |
| Total PAHs | 123 | 12 | 14 | 18 | 964 | 2.5 |

Note: units=mg/kg; NT = not tested.

**Error Two: Sample preparation procedure**
Currently there is no standardised method of preparing soil samples in the UK prior to the analysis of PAHs. The method undertaken to separate the gravel (>2 mm) from the soil (<2 mm) can include crushing, grinding, sieving or hand selection. Obviously the extent or ferocity of the grinding or crushing will influence whether clay aggregates and/or gravel size particles are broken down.

Three months into a large bioremediation project in the UK (remediating 50,000 m$^3$ of tar products plant and gas works spoil), every sample in all 15 stockpiles increased by a similar factor, particularly for 5 and 6 ring PAHs, as apparent at Day 35 in Figure 1 (data for one stockpile only). All stockpiles were influenced and then showed degradation from this unusual peak indicating this was not solely due to the nugget effect. An investigation was undertaken, which included a review of sources of error such as: non homogenous sample; sampling method; equipment; transport; laboratory preparation method; laboratory extraction methodology; and calculations. The investigation concluded that the only explanation was the sample preparation technician at the laboratory being on leave.
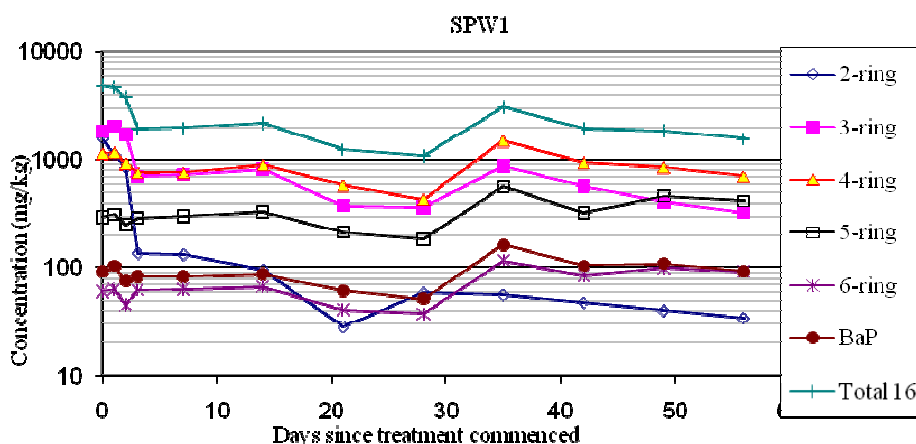


**Figure 1. PAH Degradation with time – Northern England (note: logarithmic scale on y-axis).**

To further investigate whether the presence of black carbon (i.e. ash, coke, clinker, slag and coal) being crushed during sample preparation was influencing the result of analyses, a single bulk homogenised sampled was prepared by eight methods. These eight methods were identified as potential sources of error based on observations when the samples were accompanied through the laboratory (data not shown). The eight sample preparation methods are summarised in Figure 2 with data presented in Table 2.
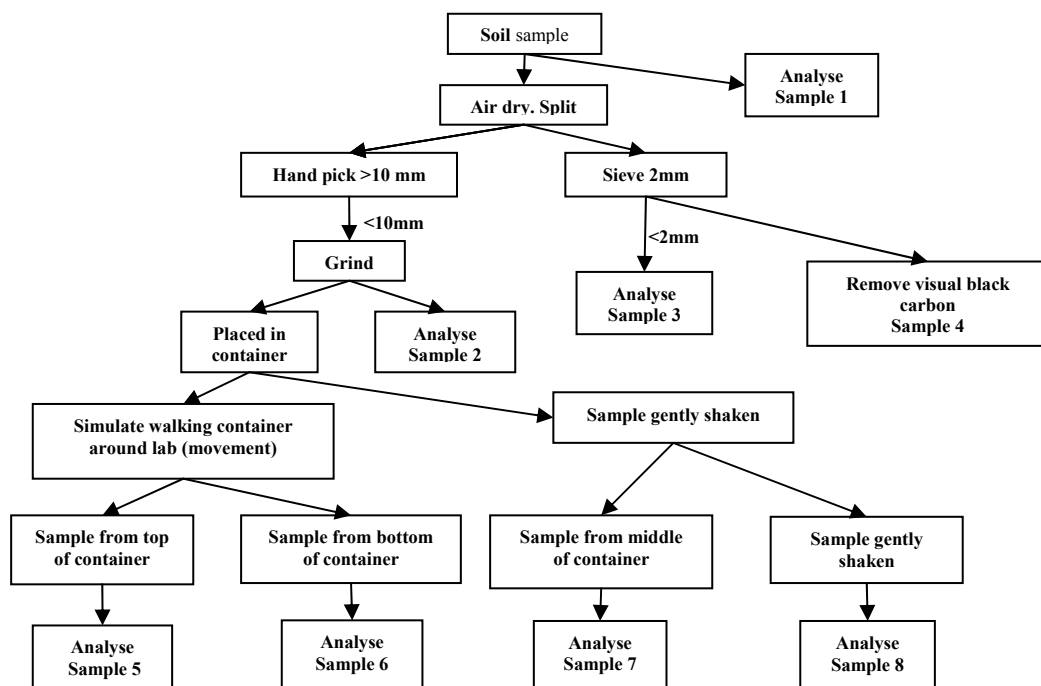


**Figure 2. Summary of sample preparation method.**

The PAH concentration ranged from 1239 (Sample 5) to 5777 (Sample 8) mg/kg from the same sample but subjected to different preparation methods (Table 2).

**Table 2. Influence of sample preparation on single sample.**

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Phenanthrene | 141 | 76 | 55 | 53 | 40 | 77 | 87 | 190 |
| Anthracene | 286 | 132 | 83 | 80 | 61 | 130 | 140 | 300 |
| Pyrene | 653 | 439 | 460 | 480 | 230 | 480 | 520 | 1100 |
| BaP | 265 | 154 | 180 | 180 | 78 | 160 | 170 | 370 |
| Total PAHs | 3494 | 2314 | 2252 | 2264 | 1239 | 2548 | 2740 | 5777 |

Note:    units=mg/kg.

**Error Three: Extraction method**

The extraction of organic compounds from soil, sediment, sludges, and waste solids can be undertaken by several methods including: (i) Soxhlet extraction (USEPA Methods 3540 and 3541) (ii) ultrasonic extraction (USEPA Method 3550); (iii) accelerated solvent extraction (USEPA Method 3545A); and (iv) steam distillation.  Currently there is no single standard method for the analysis of nonpolar trace organics

PAH contaminated material at MGP sites and most brownfield sites is not freshly contaminated but rather aged and often contains black carbon.  To investigate the impact of extraction method on the aged material we commissioned a blind trial with three laboratories using field duplicates for a gas works soil containing black carbon.  Sample preparation techniques were uniformly specified between the laboratories but extraction was not specified.  Laboratory A and B used a soxhlet extraction whilst Laboratory C used ultrasonic extraction.

The results are summarised in Table 3 and show the total PAH extracted for ultrasonic extraction ranged from 260 to 1300 mg/kg whilst the soxhlet ranged from 1374 to 2653 mg/kg.  The soxhlet extraction was 1.5 to 5.6 times more efficient than ultrasonic extraction for total PAH in the presence of black carbon and was not influenced by ring number.  This supports ASTM comments that ultrasonic extraction is less efficient with very nonpolar compounds in certain circumstances.

**Table 3.  Comparison of extraction methods.**

| Sample | SPW6A | | | SPW5A | | | SPW3A | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Extraction | Sox | Sox | U/S | Sox | Sox | U/S | Sox | Sox | Sox | U/S |
| Laboratory | A | B | C | A | B | C | A | A | B | C |
| Phenanthrene | 274 | 290 | 42 | 244 | 300 | 120 | 371 | 435 | 450 | 210 |
| Anthracene | 148 | 170 | 39 | 132 | 180 | 180 | 195 | 210 | 270 | 230 |
| Pyrene | 165 | 220 | 32 | 209 | 320 | 150 | 283 | 324 | 410 | 180 |
| BaP | 49 | 62 | 9 | 63 | 84 | 34 | 92 | 93 | 110 | 39 |
| Total PAHs | 1479 | 1577 | 260 | 1374 | 1755 | 880 | 2175 | 2351 | 2653 | 1300 |

Note: units=mg/kg; Sox = Soxhlet; U/S = Ultrasonic.

**Conclusions**

In the UK samples for analysis for metals and PAHs are prepared by air drying, removing stones (but not oversized coke) and grinding to 0.150 mm or 2 mm.  Unfortunately the grinding of coke in the sample results not only in more PAHs being analysed but also creates the opportunity for the "nugget effect" to occur, biasing the results upwards.  In summary we found that:

•    Samples are more susceptible to the "nugget effect" as treatment proceeds as residual PAHs in the soil mass have been removed by bioremediation but PAHs in coke have not.  Therefore the results depend on creating a homogenous sample and not sampling areas that have a greater amount of coke in the sub sample than is generally found within the greater mass of the sample.

•    The grinding of soil samples during laboratory preparation produces errors which are dependent on the amount and type of gravel sized fractions present.  It can act to both increase or decrease the compound concentration and thereby does not provide a reproducible representation of the environment.

•    Soxhlet extraction of samples containing Black Carbon might be too aggressive and result in the decaying or swelling of silica and some silicates thereby not providing an accurate representation of the environment.

**References**

ASTM (1996) Annual Book of ASTM Standards. (American Society of Testing and Materials: West Conshohocken, PA).

Curtis J, Narayanan R (1998) Effects of laboratory procedures on soil electrical property measurements. *Instrumentation and Measurement* **47**, 1474-1480

Don Scott H (2000) 'Soil Physics: Agricultural and Environmental Applications'. (Iowa State University Press: Iowa)

National Grid (2006) 'Methods for the Collection and Analysis of Samples from National Grid Sites'. (National Grid Property Holdings Limited: London)

Starks TH (1986) Determination of support in soil sampling. *Mathematical Geology* **18**, 529-537.

US EPA (1994) 'Method 3541, Automated Soxhlet Extraction.' In Methods for Evaluation of Solid Waste, Physical/Chemical Methods, 3rd Edition, USEPA, Office of Solid Waste and Emergency Response, Washington DC.

US EPA (1996) Method 3540C, Soxhlet Extraction. In 'Methods for Evaluation of Solid Waste, Physical/Chemical Methods'. 3rd Edition. (USEPA, Office of Solid Waste and Emergency Response: Washington, DC).

US EPA (2007) Method 3545A, Pressurized Fluid Extraction (PFE). In 'Methods for Evaluation of Solid Waste, Physical/Chemical Methods'. 3rd Edition. (USEPA, Office of Solid Waste and Emergency Response: Washington, DC).

US EPA (2007) Method 3550C, Ultrasonic Extraction. In 'Methods for Evaluation of Solid Waste, Physical/Chemical Methods'. 3rd Edition. (USEPA, Office of Solid Waste and Emergency Response: Washington, DC).

US EPA (2007) Method 3500C Organic Extraction and Sample Preparation, Revision 3. In 'Methods for Evaluation of Solid Waste, Physical/Chemical Methods'. (USEPA, Office of Solid Waste and Emergency Response: Washington DC).

Van Deuren J, Lloyd T, Chhetry S, Liou R, Peck R (2002) 'Remediation Technologies Screening Matrix and Reference Guide'.