AMELIORATING ARSENIC-CONTAMINATED SOIL WITH DIATOMITE IN RON PHIBUN DISTRICT, NAKHON SI THAMMARAT PROVINCE, THAILAND: FIELD TRIALS SET-UP

P.H. Whitbread-Abrutat\textsuperscript{1}, A. Paijitprapapon\textsuperscript{2}, P. Charoenchaisri\textsuperscript{2} and K. Atkinson\textsuperscript{1}

\textsuperscript{1} Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE, United Kingdom
\textsuperscript{2} Environment Division, Department of Mineral Resources, Rama VI Road, Ratthavee, Bangkok, 10400, Thailand

Technical Report, March 1999
AMELIORATING ARSENIC-CONTAMINATED SOIL WITH DIATOMITE IN RON PHIBUN DISTRICT, NAKHON SI THAMMARAT PROVINCE, THAILAND: FIELD TRIALS SET-UP

P.H. Whitbread-Abrutat\textsuperscript{1}, A. Paijitprapapon\textsuperscript{2}, P. Charoenchaisri\textsuperscript{2} and K. Atkinson\textsuperscript{1}

\textsuperscript{1} Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE, United Kingdom
\textsuperscript{2} Environment Division, Department of Mineral Resources, Rama VI Road, Ratthavee, Bangkok, 10400, Thailand

This document is an output from a project funded by the UK Department for International Development (DFID) under the UK provision of technical assistance to developing countries. The views expressed are not necessarily those of the Department.

\textit{DFID classification:}
Subsector: Geoscience
Theme: G2
Project title: Treatment of contaminated land using diatomite
Reference number: R6488

\textit{Bibliographic reference:}
CSM Technical Report, Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE, UK

\textit{Keywords:}
potentially toxic elements, heavy metals, porewater, mining, mineral-processing

\textit{Cover plate:}
Incorporation of diatomite into contaminated soil in one of the trial plots during preparation of the long term field experiment in Ron Phibun village
SUMMARY

This report describes the setting-up of a long term field investigation into the efficacy of treating As-contaminated land with the industrial mineral diatomite. Previous work in this three-year project identified a sample of diatomite that was potentially suitable for the amelioration of metalliferous mine wastes. The field trials described herein were set-up in December 1998.

An area of land adjacent to an abandoned ore-dressing plant in Ron Phibun village, Nakhon Si Thammarat Province, southern Thailand, known to be contaminated with As and other PTEs, was chosen as the field site. Before setting-up the experiment, the site was cleared of vegetation and refuse. Twenty 1.5 m x 1.5 m plots were laid out. Each plot was then homogenised by hand to reduce variation in soil chemical and physical properties. The experiment was designed as a fully randomised block with three application rates of diatomite plus a control, each replicated five times. Diatomite application rates were calculated from rates previously used in pilot scale column leaching experiments and adapted to a soil depth of 30 cm (the maximum depth to which diatomite was incorporated). The diatomite was applied by hand at rates (including the corresponding mass applied in each case) of: 0% (control), 2.5% (20.6 kg), 5% (41.2 kg) and 10% (82.5 kg).

Soil samples were taken from each plot before and after the addition of diatomite for subsequent chemical analysis. Twenty samplers, designed to extract in situ soil porewaters for analysis, were fabricated at CSM to a unique design. Full design, construction, installation and operational details for the soil porewater samplers are provided in this report. One porewater sampler was installed in the centre of each plot. The soil samples taken before the addition of diatomite were digested by modified aqua regia and analysed by atomic absorption spectrophotometry to determine "total" concentrations of each element. Both pre- and post-diatomite soil samples were analysed for their water soluble concentrations of As, Cd, Cu, Fe, Mn, Pb and Zn. Soil porewaters were sampled the day after the installation of the porewater samplers.

Taken as whole, the field site was shown to be geochemically heterogeneous with a hot-spot of high PTE concentrations running through the site producing very high PTE concentrations in the corresponding field plots. Statistical comparisons made between the different diatomite application rates (using the Kruskal-Wallis non-parametric method) showed no significant differences between treatments. These results were mirrored in the analysis of the soil porewaters taken the day after the installation of the samplers. The differences between treatments in soil porewater element concentrations were much less marked than for the soil "total" element results.

At the time of writing (March 1999), only one set of porewater results has so far been received. Consequently, it is too early to derive firm conclusions regarding the use diatomite as an ameliorant for As-contaminated soils. The field experiments are will be monitored monthly for one year in the first instance. A monthly record of vegetation cover is also being made. The soil porewater sampling technology is a cheap and easy to construct and operate technology that could and should be used more widely for the sampling of soil porewaters, for example in agricultural and ecological contexts. Similarly, this design of field experiment is a simple and statistically rigorous means of investigating the actions of a wide variety of soil amendments, including other industrial minerals, fertilisers and organic soil improvers.

This report is an output from a three-year collaborative project entitled “Treatment of contaminated land using diatomite” between Camborne School of Mines (CSM) of the University of Exeter, UK, the British Geological Survey (BGS), UK and the Department of Mineral Resources (DMR) of the Government of Thailand. The work was funded by the Department for International Development (DFID) of the British Government under their Knowledge and Research (KAR) programme (project number R6488). Invaluable logistical support was provided by DMR, Government of Thailand.
CONTENTS

1 INTRODUCTION .................................................................................................................. 1
   1.1 Background .................................................................................................................. 1
   1.2 Overview of the experiment ......................................................................................... 2

2 METHODS ..................................................................................................................................... 2
   2.1 Site preparation and experimental set-up ....................................................................... 2
   2.2 Sampling and sample analysis ...................................................................................... 3
   2.3 Statistical analysis ....................................................................................................... 3

3 RESULTS .................................................................................................................................... 10
   3.1 Field site soil properties ............................................................................................. 10
   3.2 Soil porewater chemistry ........................................................................................... 10

4 DISCUSSION AND CONCLUSIONS ..................................................................................... 17
   4.1 Further investigations .................................................................................................. 17

5 ACKNOWLEDGEMENTS ........................................................................................................ 18

6 REFERENCES .......................................................................................................................... 18

APPENDIX A1: SOIL POREWATER SAMPLERS ........................................................................ 19
   A1.1 Construction details .................................................................................................. 19
   A1.2 Installation instructions ............................................................................................. 19
   A1.3 Operation .................................................................................................................. 21

APPENDIX A2: CHEMICAL ANALYTICAL METHODOLOGY .................................................... 22
   A2.1 Aqua regia digestion .................................................................................................. 22

LIST OF FIGURES

Figure 2.1: Sketch map of the field trials set-up showing the locations of randomised treatment plots. Plots 1-5, 0% diatomite; plots 6-10, 2.5% diatomite (20.6 kg); plots 11-15, 5% diatomite (41.2 kg); plots 16-20, 10% diatomite (82.5 kg) .............................................................. 9

Figure 3.2: Distribution of “total” soil As concentrations over the field site, based on soil samples taken from individual field plots. .................................................................................. 12

Figure 3.3: Distribution of “total” soil Cd concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 12

Figure 3.4: Distribution of “total” soil Cu concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 13

Figure 3.5: Distribution of “total” soil Fe concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 13

Figure 3.6: Distribution of “total” soil Mn concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 14

Figure 3.7: Distribution of “total” soil Pb concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 14

Figure 3.8: Distribution of “total” soil Zn concentrations over the field site, based on soil samples taken from individual field plots .................................................................................. 14

Figure A1.1: Schematic diagram of a soil porewater sampler. For construction details see appendix A1.1 ................................................................................................................................. 20

Figure A1.2: Stylised representation of the set-up required to extract porewater from the porewater sampler. For mode of operation see appendix A1.3 ........................................................................... 21
LIST OF TABLES

Table 3.1: "Total" element concentrations of field site soil based on results of modified aqua regia digestion (mean ± sd, range, n = 20) and compared with values for typical uncontaminated soils ................................................................. 10

Table 3.2: Comparison of the "total" element concentrations (based on a modified aqua regia digestion) of field site soil samples from each field plot prior to the application of diatomite, classified by the intended diatomite application rate (in µg g⁻¹ unless otherwise stated, mean ± sd and range, n = 5). Statistical comparisons were made using the Kruskal-Wallis test ........................................................................................................... 11

Table 3.3: Comparison of soil porewater results for each diatomite application rate for the first sampling period (December 1998; in µg m⁻¹; mean, sd and range, n = 5). Statistical comparisons were made using the Kruskal-Wallis test ........................................................................................................... 16

LIST OF PLATES

Plate 2.1: The field trials site in Ron Phibun village prior to site clearance ...................................................... 4
Plate 2.2: Clearing the site of vegetation and assorted rubbish ............................................................................. 4
Plate 2.3: The cleared site before delineation of the field plots ............................................................................. 5
Plate 2.4: Delineation of the plots followed by homogenisation of the soil in each plot ................................... 5
Plate 2.5: Soil porewater samplers ......................................................................................................................... 6
Plate 2.6: Installation of a soil porewater sampler. A fine silica sand sludge is added first to cover the ceramic end-piece ....................................................................................................................... 6
Plate 2.7: Part of the completed field site. Note the porewater sampler in the centre of each plot ................. 7
Plate 2.8: Creating a vacuum in the sampler using a hand-pump prior to extracting the soil porewater ........................................................................................................................................ 7
Plate 2.9: The set-up for removing the soil porewater from the porewater sampler ........................................ 8
1 INTRODUCTION

1.1 Background
Metalliferous mines are commonly associated with elevated concentrations of potentially toxic elements (PTEs) in both the wastes that they produce or in the soils surrounding them. This presents a common and serious environmental problem in many parts of the world. PTEs are elements that may or may not be beneficial to organisms at very low concentrations, but are toxic at relatively low concentrations. The term "PTE" can include a variety of otherwise unrelated elements and is superseding the more etymologically ambiguous term "heavy metals". For the purposes of this report, the term PTE refers to the elements As, Cd, Cu, Mn, Pb and Zn. Fe was also investigated.

Tin mining and processing wastes in the vicinity of Ron Phibun village, Nakhon Si Thammarat Province, southern Thailand, are known to be enriched in As and other PTEs (Jariyawat and Piyawong, 1993; Fordyce et al., 1995; Williams et al., 1996). This, coupled with the documented chronic arsenic-related health problems of the Ron Phibun area and the existence of nationally available diatomite deposits in northern Thailand has provided an opportunity to develop a long term investigation into the novel aspect of ameliorating As-contaminated land with diatomite.

Camborne School of Mines (CSM), University of Exeter has been at the forefront of research into reducing the environmental impact of mining and beneficiation wastes for over a decade. The main thrust of this research has been in the novel field of applying industrial minerals to contaminated land in and around derelict metal mine sites in order to reduce the availability of inorganic contaminants. A variety of industrial minerals are potentially useful for this purpose (e.g. Mitchell, 1991; Gworek, 1992a,b) and diatomite has been identified as one of the most promising (Atkinson et al., 1990; Mitchell & Atkinson, 1991; Abrutat et al. 1994; Whitbread-Abrutat, 1995).

Diatomite (also known as diatomaceous earth and kieselguhr) is a naturally occurring form of biogenic silica produced by phytoplanktonic organisms. It occurs as economically viable geological deposits in many parts of the world and is used as an industrial mineral, primarily as a filter aid in beer and wine processing and for clarifying edible oils. To a lesser extent it is also used as fillers in paper, paint and plastics, as an absorbent and as an abrasive. Competition from other industrial minerals has caused a decline in the importance of diatomite in its traditional fields, but potential new markets are now developing, particularly in the biotechnology and hazardous waste treatment industries (Harries-Rees, 1994). Previous work at CSM and DMR relating to the current project has shown that the addition of diatomite to PTE-rich mine wastes in pilot scale column leaching experiments can significantly reduce the concentrations of As and other PTEs in the leachate emanating from the columns (Whitbread-Abrutat et al., 1999).

The implementation of field trials was the final stage of the three-year project "Treatment of contaminated land using diatomite", funded by the Department for International Development's Knowledge and Research (DFID-KAR) programme (project number R6488) of the British Government. This project was a collaborative venture between Camborne School of Mines (CSM), of the University of Exeter, UK, the British Geological Survey (BGS) and the Department of Mineral Resources (DMR) of the Government of Thailand. The first phase of the project involved intensive studies of PTE-contaminated substrates collected from various metalliferous mining areas in southern Thailand (Whitbread-Abrutat et al., 1997a,b). The second phase investigated the efficacy of diatomite (from northern Thailand)
in reducing PTE mobility in two different PTE-contaminated mine wastes from southern Thailand using laboratory-based column leaching experiments (Whitbread-Abrutat et al., 1999). This report describes the setting-up of, and preliminary results from, the long term field trials and the implementation of a monitoring regime in the village of Ron Phibun.

1.2 Overview of the experiment

The primary objective was to set-up a long term field experiment to evaluate the efficacy of diatomite in ameliorating PTE concentrations in a highly contaminated soil. This extends the work (unpublished) started by CSM in Cornwall, UK, on establishing long term field trials to investigate the efficacy of industrial minerals in ameliorating contaminated soils.

A site containing soil known to be highly contaminated with PTEs was chosen behind the now abandoned processing plant in Ron Phibun village, Nakhon Si Thammarat Province, Thailand. Diatomite application rates were chosen for the experiment based on experience gained from the column-leaching experiments (Whitbread-Abrutat et al., 1999). The maximum rate of 10% diatomite was decided upon largely according to subjective economic considerations: for treating large areas, the application of high rates of diatomite would entail considerable expense in transport and incorporation owing to the high volume per unit mass of diatomite. It was decided that a rate greater than 10% would probably be uneconomical and/or impractical to apply when the full scale field application of this rate is considered.

The choice of diatomite for the field experiment was made based on intensive physical, chemical and mineralogical analyses of several different diatomites collected from Lampang Province, northern Thailand (Inglethorpe et al., 1998, 1999) and simple jar tests investigating the As uptake properties of each diatomite sample.

In order to sample *in situ* soil porewaters, soil porewater samplers (or suction lysimeters) were constructed and installed in each plot. These enabled the sampling of soil porewaters on demand for the subsequent analysis of pH, conductivity, oxidation-reduction potential (ORP) and the concentrations of the elements As, Cd, Cu, Fe, Mn, Pb and Zn.

2 METHODS

2.1 Site preparation and experimental set-up

The field site was located immediately north-west of, and adjacent to, the abandoned processing plant situated in the town of Ron Phibun. Before the diatomite could be incorporated into the field plots, the site had to be cleared of vegetation and large obstacles (plates 2.1 to 2.3). The plots were then delineated, avoiding any remaining immovable obstacles. Twenty 1.5 m x 1.5 m plots were delineated (figure 2.1). Prior to addition of the diatomite, each plot was cultivated to a depth of 30 cm and thoroughly homogenised to reduce spatial heterogeneity in soil chemical and physical properties (plate 2.4). At this stage five sub-samples of soil were taken from each plot and bulked to produce approximately 1 kg of soil per plot for subsequent chemical analysis.

Three diatomite application rates were chosen: 2.5%, 5% and 10% and a control (0% diatomite). The actual weights of diatomite applied per field plot were derived from scaling up the diatomite application rates as used in the column-leaching experiments (Whitbread-Abrutat et al., 1999) and adapted to apply to a depth of 30 cm (the depth to which it is most easy to mix the soil by hand). The application rates and the corresponding diatomite weights were 0% (0 kg, control), 2.5% (20.6 kg), 5% (41.2 kg) and 10% (82.5 kg). The appropriate quantity of diatomite was then added to each plot and mixed into the soil thoroughly by hand.
to a depth of 30 cm (see cover plate). The 0% treatment was treated similarly despite possessing no diatomite. Soil samples were taken again from each plot for chemical analysis.

Each treatment was replicated five times and the whole experiment was designed as a fully-randomised block to provide statistical robustness to cope with any variation in soil characteristics. One soil porewater sampler was installed in the centre of each plot (plates 2.5 and 2.6; see appendix A1 for detailed construction and field-installation instructions). Plate 2.6 shows part of the completed field site.

2.2 Sampling and sample analysis

Substrate samples were taken as described above, both before and after the addition of diatomite. All chemical analyses were undertaken by Mineral Analysis Division, DMR. Samples were prepared by air-drying to constant weight and then sieving to <2 mm. Approximately 50 g of the <2 mm fraction was riffled out and ground to a floury texture.

The first set of samples was analysed for their "total" element concentrations (the precise methodology is provided in appendix A2). Other parameters investigated included pH, conductivity and ORP.

Soil porewaters are being sampled monthly initially (plates 2.7 and 2.8). Measurements of pH, conductivity and oxidation-reduction potential (ORP) are made as soon as possible after collection before acidifying with concentrated nitric acid to preserve the samples prior to further analyses. Porewater samples are being analysed for As, Cd, Cu, Fe, Mn, Pb and Zn by atomic absorption spectrometry (AAS) (and hydride generation AAS in the case of As). Monthly records of the ground vegetation cover are also being made.

2.3 Statistical analysis

Visual analysis of the standard deviations of the "total" element content of the field site soils and the soil porewater results indicated that these results were not normally distributed. Consequently, soil and soil porewater chemistry results from the different treatment plots were compared by the Kruskal-Wallis test which is essentially the non-parametric analogue of the oneway-ANOVA test and compares the variables under consideration by rank order rather than by means.

---

1 refers to sample digestion by a modified aqua regia method
Plate 2.1: The field trials site in Ron Phibun village prior to site clearance

Plate 2.2: Clearing the site of vegetation and assorted rubbish
Plate 2.3: The cleared site before delineation of the field plots

Plate 2.4: Delineation of the plots followed by homogenisation of the soil in each plot
Plate 2.5: Soil porewater samplers

Plate 2.6: Installation of a soil porewater sampler. A fine silica sand sludge is added first to cover the ceramic end-piece
Plate 2.7: Part of the completed field site. Note the porewater sampler in the centre of each plot.

Plate 2.8: Creating a vacuum in the sampler using a hand-pump prior to extracting the soil porewater.
Plate 2.9: The set-up for removing the soil porewater from the porewater sampler
Figure 2.1: Sketch map of the field trials set-up showing the locations of randomised treatment plots. Plots 1-5: 0% diatomite; plots 6-10: 2.5% diatomite (20.6 kg); plots 11-15: 5% diatomite (41.2 kg); plots 16-20: 10% diatomite (82.5 kg).
3 RESULTS

The field trials were set-up in the middle of December 1998, two-and-a-half months before the time of writing, consequently relatively few results are currently available for discussion. Results that are available at the time of writing are the "total" element contents of the field site soil and the first month's porewater samples.

3.1 Field site soil properties

Based on simple field observations prior to field plot preparation, the soil of the field site, once cleared, was shown to be very heterogeneous in physical properties (colour and compaction) on a scale of decimetres. The area had obviously been used as a small-scale municipal dump for many years, including the dumping of mineral-processing wastes from the ore-dressing plant adjacent to the field site (figure 2.1). The field area contained elevated concentrations of all the elements investigated when compared to the values expected in a normal, uncontaminated soil (table 3.1).

Table 3.1: "Total" element concentrations of field site soil based on results of modified aqua regia digestion (mean ± sd, range, n = 20) and compared with values for typical uncontaminated soils.

<table>
<thead>
<tr>
<th>Element</th>
<th>Units</th>
<th>Mean</th>
<th>sd</th>
<th>Range</th>
<th>Typical soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>µg g⁻¹</td>
<td>6510</td>
<td>7074</td>
<td>300-22000</td>
<td>0.5-30</td>
</tr>
<tr>
<td>Cd</td>
<td>µg g⁻¹</td>
<td>10.5</td>
<td>10.1</td>
<td>1.0-29.4</td>
<td>0.03-0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>µg g⁻¹</td>
<td>105</td>
<td>75.3</td>
<td>21-223</td>
<td>5-80</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
<td>4.85</td>
<td>2.69</td>
<td>1.83-10.7</td>
<td>0.02-10</td>
</tr>
<tr>
<td>Mn</td>
<td>µg g⁻¹</td>
<td>5720</td>
<td>5215</td>
<td>800-17900</td>
<td>50-2000</td>
</tr>
<tr>
<td>Pb</td>
<td>µg g⁻¹</td>
<td>666</td>
<td>648</td>
<td>55-1700</td>
<td>2-20</td>
</tr>
<tr>
<td>Zn</td>
<td>µg g⁻¹</td>
<td>330</td>
<td>123</td>
<td>128-564</td>
<td>10-300</td>
</tr>
</tbody>
</table>

Field site heterogeneity was reflected in the variation of chemical properties across the site (table 3.2; figures 3.2 to 3.8). An examination of the spatial distribution of each element based on individual plot soil chemistry prior to the application of diatomite identified two "hot-spots" of very high "total" concentrations for As, Cd, Fe, Mn and Pb, with elevated (but lower) concentrations of Cu and Zn, centred on plots 1, 10, 16 and 6 and plots 15 and 7.

These hot-spots may, in reality, be one hot-spot elongated along a NW-SE trending axis. Such heterogeneity in an experiment such as this one precludes the parametric statistical analysis of variance, consequently non-parametric methods must be used. Statistical comparison of the "total" element concentrations of the field plots using the Kruskal-Wallis test showed that there were no significant differences (at \( p<0.05 \)) between element concentrations in plots designated to receive specific diatomite application rates (table 3.2). This indicates that over each group of five replicates per intended diatomite addition rate, the differences in element concentration between each group were statistically negligible.

3.2 Soil porewater chemistry

The first series of samplers from the soil porewater samplers were taken on 12 December 1998, the day after their installation. These results are summarised in table 3.3. Statistical analysis of these results showed that the different diatomite application rates produced no significant differences (at \( p<0.05 \)) in the porewater concentrations of the elements investigated. A period of several days or weeks may be required for the actions of the diatomite to become apparent and for the oxidation of newly exposed sulphide minerals to cause a detectable increase in the release of PTEs.
Table 3.2: Comparison of the "total" element concentrations (based on a modified aqua regia digestion) of field site soil samples from each field plot prior to the application of diatomite, classified by the intended diatomite application rate (in µg g⁻¹ unless otherwise stated, mean ± sd and range, n = 5). Statistical comparisons were made using the Kruskal-Wallis test.

<table>
<thead>
<tr>
<th>Element</th>
<th>0%</th>
<th>sd</th>
<th>range</th>
<th>2.5%</th>
<th>sd</th>
<th>range</th>
<th>5%</th>
<th>sd</th>
<th>range</th>
<th>10%</th>
<th>sd</th>
<th>range</th>
<th>Signif. level</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>6820</td>
<td>8903</td>
<td>300-22000</td>
<td>6420</td>
<td>8900</td>
<td>400-17500</td>
<td>5020</td>
<td>7430</td>
<td>400-17700</td>
<td>7780</td>
<td>7119</td>
<td>300-16700</td>
<td>ns</td>
</tr>
<tr>
<td>Cd</td>
<td>9.32</td>
<td>11.6</td>
<td>1.3-29.4</td>
<td>12.9</td>
<td>10.4</td>
<td>1.4-21.7</td>
<td>8.10</td>
<td>10.1</td>
<td>1.4-24.7</td>
<td>11.8</td>
<td>10.9</td>
<td>1.0-26.7</td>
<td>ns</td>
</tr>
<tr>
<td>Cu</td>
<td>87.8</td>
<td>79.3</td>
<td>31-223</td>
<td>126</td>
<td>91.1</td>
<td>21-206</td>
<td>92.0</td>
<td>67.6</td>
<td>35-201</td>
<td>113</td>
<td>81.0</td>
<td>24-215</td>
<td>ns</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>4.14</td>
<td>2.23</td>
<td>2.13-7.78</td>
<td>6.11</td>
<td>3.93</td>
<td>1.83-10.74</td>
<td>4.21</td>
<td>1.99</td>
<td>2.56-7.43</td>
<td>4.93</td>
<td>2.62</td>
<td>2.35-7.73</td>
<td>ns</td>
</tr>
<tr>
<td>Mn</td>
<td>4400</td>
<td>4339</td>
<td>1100-11700</td>
<td>8540</td>
<td>7720</td>
<td>800-17900</td>
<td>4300</td>
<td>3724</td>
<td>1000-10500</td>
<td>5640</td>
<td>4714</td>
<td>1400-10700</td>
<td>ns</td>
</tr>
<tr>
<td>Pb</td>
<td>524</td>
<td>622</td>
<td>100-1600</td>
<td>904</td>
<td>833</td>
<td>73-1700</td>
<td>438</td>
<td>519</td>
<td>96-1300</td>
<td>708</td>
<td>645</td>
<td>55-1600</td>
<td>ns</td>
</tr>
<tr>
<td>Zn</td>
<td>306</td>
<td>110</td>
<td>195-477</td>
<td>335</td>
<td>154</td>
<td>175-564</td>
<td>345</td>
<td>122</td>
<td>196-439</td>
<td>336</td>
<td>142</td>
<td>128-476</td>
<td>ns</td>
</tr>
</tbody>
</table>

sd, standard deviation
*significance level at p < 0.05; ns, not significant
Figure 3.2: Distribution of "total" soil As concentrations over the field site, based on soil samples taken from individual field plots.

Figure 3.3: Distribution of "total" soil Cd concentrations over the field site, based on soil samples taken from individual field plots.
Figure 3.4: Distribution of "total" soil Cu concentrations over the field site, based on soil samples taken from individual field plots.

Figure 3.5: Distribution of "total" soil Fe concentrations over the field site, based on soil samples taken from individual field plots.
Figure 3.6: Distribution of "total" soil Mn concentrations over the field site, based on soil samples taken from individual field plots.

Figure 3.7: Distribution of "total" soil Pb concentrations over the field site, based on soil samples taken from individual field plots.
**Figure 3.8:** Distribution of "total" soil Zn concentrations over the field site, based on soil samples taken from individual field plots.
Table 3.3: Comparison of soil porewater results for each diatomite application rate for the first sampling period (December 1998; in μg ml⁻¹; mean, sd and range, n = 5). Statistical comparisons were made using the Kruskal-Wallis test.

<table>
<thead>
<tr>
<th>Element</th>
<th>0%</th>
<th>sd</th>
<th>range</th>
<th>2.5%</th>
<th>sd</th>
<th>range</th>
<th>5%</th>
<th>sd</th>
<th>range</th>
<th>10%</th>
<th>sd</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.236</td>
<td>0.029</td>
<td>0.21-0.28</td>
<td>0.196</td>
<td>0.26</td>
<td>0.03-0.63</td>
<td>0.186</td>
<td>0.077</td>
<td>0.05-0.24</td>
<td>0.133*</td>
<td>0.07</td>
<td>0.04-0.21</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>0.012</td>
<td>&lt;0.01-0.03</td>
<td>0.004</td>
<td>0.009</td>
<td>&lt;0.01-0.02</td>
<td>0.006</td>
<td>0.009</td>
<td>&lt;0.01-0.02</td>
<td>0.008</td>
<td>0.008</td>
<td>&lt;0.01-0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>0.256</td>
<td>0.346</td>
<td>0.05-0.87</td>
<td>0.206</td>
<td>0.268</td>
<td>0.06-0.68</td>
<td>0.152</td>
<td>0.153</td>
<td>0.04-0.42</td>
<td>0.146</td>
<td>0.139</td>
<td>0.05-0.38</td>
</tr>
<tr>
<td>Mn</td>
<td>0.152</td>
<td>0.207</td>
<td>0.04-0.52</td>
<td>0.084</td>
<td>0.031</td>
<td>0.05-0.11</td>
<td>0.09</td>
<td>0.049</td>
<td>0.06-0.15</td>
<td>0.138</td>
<td>0.013</td>
<td>0.12-0.15</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.02</td>
<td>-</td>
<td>-</td>
<td>&lt;0.02</td>
<td>-</td>
<td>-</td>
<td>&lt;0.02</td>
<td>-</td>
<td>-</td>
<td>&lt;0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>0.45</td>
<td>0.823</td>
<td>0.05-1.92</td>
<td>0.12</td>
<td>0.07</td>
<td>0.04-0.19</td>
<td>0.134</td>
<td>0.101</td>
<td>0.03-0.28</td>
<td>0.29</td>
<td>0.192</td>
<td>0.11-0.56*</td>
</tr>
</tbody>
</table>

sd, standard deviation
* n = 4
* significance level at p<0.05; ns, not significant

Signif. level:
ns
4 DISCUSSION AND CONCLUSIONS

The field site has been shown to be geochemically very heterogeneous, but by the judicious use of non-parametric methods of statistical comparison, the effects of this heterogeneity have been reduced without adversely affecting the overall significance of the results. The one minor drawback with the Kruskal-Wallis test is that it is slightly less rigorous in some situations when compared to the equivalent oneway ANOVA parametric method.

The field trials site is contaminated with elevated concentrations of all the elements investigated. However, the contamination is not homogeneously distributed across the site but appears to be confined to a particular "hot-spot" area. The porewater samples taken from the plots within this "hot-spot", at least for the first period of sampling, are generally not significantly higher than those taken from without. This leads to the tentative conclusion that much of the soluble element content has been leached from the soil (which appeared to have been undisturbed for a considerable period of time prior to clearance of the site during the setting-up of the field trials), while the remaining element content occurs as primary (unoxidised) and secondary (oxidised) minerals. Disturbance of the soil during the setting-up of the plots will have redistributed unoxidised primary minerals closer to the soil surface with a concomitant increase in soil permeability to water and air. Consequently, it can be predicted that both factors will lead to an increase in primary mineral weathering with a corresponding increase in soil porewater element concentrations over the coming months.

The first set of porewater results indicated no significant differences in element concentrations between different diatomite application rates for any of the elements investigated, but it is anticipated that significant differences will emerge over the coming months.

Soil porewater samplers constructed around a porous ceramic cup, have traditionally been used in the monitoring of soil salinity and nitrate-N, P and K concentrations in irrigated soils. Their use in the investigation of PTE concentrations in contaminated soils was pioneered at CSM by Waller (1995), and has been developed further during the course of this current work. During the short duration of the current field trials experiment, the porewater samplers have proved to be very useful in the sampling of in situ soil porewaters. Their sampling capability is naturally limited by the availability of water in the soil, but PTE mobilisation is not a problem in dry soils. The attraction of this technology for this type of work in developing countries is that the samplers are relatively cheap and easy to construct, operate and repair. The lack of moving parts, complicated structures and chemically-resistant materials ensures their longevity even in chemically harsh soils.

4.1 Further investigations

The intention is to monitor the field plots for at least one year in the first instance. As the field experiment was set-up near the end of the current project, it is recommended that a follow-up visit is made by the UK counterparts at the end of the first year of the field trials (late 1999 - early 2000) to assist in the analysis and interpretation of the large database of results that will exist by that time.

In the near future, DMR intends to sink several shallow boreholes in the vicinity of field plots to enable the monitoring of the local groundwater table. Local precipitation will also be recorded and the results will be utilised during the interpretation of the soil porewater results.

This type of field experiment and the equipment developed for it can be used to assess a variety of potential soil amendments, not just to remediate contaminated land, but also to
monitor the effects of potentially useful fertiliser materials (organic and inorganic) for agricultural purposes.

The use of diatomite in remediating contaminated land may prove potentially useful, however, financial considerations will determine whether or not the technology is economically practicable on a larger scale. Further work is required to determine the comparative economic costs of using diatomite when compared to other remediation techniques, e.g. the use of lime, soil-washing, etc., while simultaneously bearing in mind the relative effectiveness of the treatments. Investigations should also be made of the potential social impact of the diatomite land remediation technology.

5 ACKNOWLEDGEMENTS

PHWA would like to thank the staff of Environment Division, DMR, for their generous hospitality and the help extended to him during visits to Thailand concerned with this work. Camborne School of Mines workshop technical staff are cordially acknowledged for their help and advice concerning construction of the soil porewater samplers.

The authors would like to extend their gratitude to DFID of the UK Government who funded this project under their KAR programme.

6 REFERENCES


APPENDIX A1: SOIL POREWATER SAMPLERS

### A1.1 Construction details

1. Cut a 200 mm length of 44 mm internal diameter PVC pipe.
2. Turn one end on a lathe to fit tightly over the end of a ceramic pot (model 0653X01-B1M3, rated at 1 bar, high flow air entry; supplied by Soilmoisture Equipment Corp., 801 South Kellogg Avenue, Goleta, Ca. 93117, USA (WWW: http://www.soil.moisture.com).
3. Seal this join with high modulus silicone sealant.
4. Drill two holes through a rubber stopper (47 mm wide end, 41 mm narrow end). Insert two glass tubes through these holes in the rubber stopper to produce an air-tight fit.
5. Cut four lengths of flexible PVC tubing (nalgene, 3.2 mm bore). One length should be long enough to reach the bottom of the sampler. The other length can be much shorter. Set-up the tubing as shown in figure A1.1.

### A1.2 Installation instructions

1. Soak the ceramic pot part of the samplers in an upright position in water during preparation of the hole.
2. Make up a slurry of fine silica sand and water to a consistency between double cream and thick custard, i.e. still able to flow when poured down the hole.
3. Auger a hole to the correct depth (*circa* 25-28 cm). Keep the sub-soil and top-soil separate (if appropriate).
4. Pour sufficient slurry down the hole to cover the pot. If the slurry is of the right consistency, it will run down the side of the hole, reach the bottom and cover the ceramic pot. Check that the top of the ceramic end-piece is covered with slurry.
5. Apply a vacuum to the pump using a hand pump. The draws the slurry around the ceramic pot ensuring good contact.

19
6. Back-fill the hole with parent soil material in small quantities, re-packing with a stick.
7. Introduced bentonite to act as a water tight plug (if appropriate) just below the soil surface.
8. (Optional). Place a square of chicken wire just below soil surface, over the porewater sampler, to enable easy detection by a metal detector. Record the position (and GPS) on a map.
9. Finish re-packing the soil.
10. Remove the vacuum and suck out the solution that will have collected.
11. Clip and leave. Installation is now complete.

Figure A1.1: Schematic diagram of a soil porewater sampler. For construction details see appendix A1.1.
A1.3 Operation

1. Set-up the sampling equipment as shown in figure A1.2.
2. Loosen clip A and tighten clip B. Attach hand-pump to tube A and apply suction to 0.5-0.6 bar. 15 to 20 minutes should be adequate time for the movement of sufficient porewater from the soil into the sampler.
3. Close clip A.
4. Attach pump at tube C and apply suction.
5. Open clip B. Collect sample, allowing overflow to collect in the trap. If necessary, open clip A slowly to flush out the sampler until all the water has been removed. Remove sample bottle and take sample for analysis. Substitute a clean sample bottle ready for the next porewater sampler.

Figure A1.2: Stylised representation of the set-up required to extract porewater from the porewater sampler. For mode of operation see appendix A1.3
APPENDIX A2: CHEMICAL ANALYTICAL METHODOLOGY

A2.1 Aqua regia digestion

1. Weigh out approximately 1 g of sample into a 250 ml beaker. Add 20 ml of concentrated nitric acid and reduce to half of the original volume on a hot-plate.

2. Add 10 ml of concentrated hydrochloric acid and boil until no more dense brown fumes are produced.

3. Filter through a no. 42 filter paper and dilute to 100 ml.

4. Analyse by AAS / GFAAS.