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Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils

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ABSTRACT

Cement or lime can be used to treat trace element contaminated soils, reducing their mobility due to increased soil pH which enhances precipitation and adsorption, and also due to pozzolanic reactions and cementation. In the present work, an alkaline and an acidic soil both containing Cd, Co, Cu, Ni, Pb, Sb and Zn from either geogenic or geogenic and anthropogenic origin were treated with cement or calcium hydroxide. Soils were then extracted with dilute HNO_3 or NaOH solution of different concentrations to obtain extracts of different pH (pH 4–12). In untreated soils, Co, Cu, Ni and Pb in solutions were detected at alkaline pH. The addition of cement or $Ca(OH)_2$ reduced the mobility of every trace element at high pH, but enhanced the mobility of Cd, Co, Cu, Ni, Pb and Zn at low pH. Metal mobilisation at high pH was observed for Cu in the acidic soil due to the liberation of dissolved organic matter. Below pH 6, Sb mobility was lower in the cement-treated soil compared to the untreated soil, but the same in the $Ca(OH)_2$ treated soil as in the control soil. Comparison with theoretical trace element precipitates suggested that the mobility of trace elements is likely reduced at high pH by encapsulation and immobilisation within the cement matrix rather then precipitation.

1. Introduction

Using cement as a remediation agent for contaminated sites raises soil pH, increasing metal adsorption and/or precipitation. Cement may also reduce trace element mobility further due to encapsulation as well as various interactions of the trace element with cement hydration products, including adsorption, co-precipitation, inclusion (micro encapsulation) and chemical incorporation into the hydrated cement matrix [1]. Some of these mechanisms could also be effective at lower pH. For example, it was shown that Si from the cement matrix did not significantly leach above pH 6 [2,3].

Lime can be used to increase soil pH, reducing trace element mobility and bioavailability [4,5] due to enhanced adsorption and/or precipitation. As well, when sufficient lime is added to the soil, $Ca(OH)_2$ will react with water and pozzolans to form cementitious products such as calcium aluminate hydrates or calcium sulphoaluminate similar to ettringite in the presence of sulphate [6]. The reactions are similar to those for cement, but require the dissolution of silica and alumina from soil. This pozzolanic reaction forms a tough, water soluble gel which cements soil particles together [6], potentially affecting trace element mobility as described for cement.

Extensive literature exists on trace element leaching and immobilisation mechanisms in cement paste or wastes [3,7–10]. However, few authors have investigated the effect of cement (or $Ca(OH)_2$) on soils and even fewer on soils with trace elements from anthropogenic sources; most studies have used artificial and/or contaminant-spiked soils. By using field contaminated soils, conclusions drawn from the studies are less likely to be biased by the chemical behaviour of mono-speciated soluble trace elements, which are typically used in spiking experiments. Because pH dominates the control of trace element mobility [11,12], and because the pH of the treated soil can change over time, evaluating the leaching behaviour as a function of pH covers a wide range of environmentally relevant conditions and thus is a good basis for evaluation of environmental performance [12–14].

In this paper, soils from two different sites that contain Cd, Co, Cu, Ni, Pb, Sb and Zn from geogenic, or geogenic and anthropogenic origin, were studied; these materials have been rarely studied before, thus the present data describing metal mobility as a function of remediation, are novel. The mobility of those trace elements was measured after cement or calcium hydroxide amendment as a

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Table 1
Physical and chemical characteristics of soils, cement and $Ca(OH)_2$.

Parameters	SO	NO	Cement	$Ca(OH)_2$
pH	8.2 (0.017)	4.55 (0.019)	n.a.	n.a.
E.C. (μS cm^{-1})	222 (12)	92 (0.78)	n.a.	n.a.
C.E.C. (Cmol(+) kg^{-1})	7.10 (0.24)	1.98 (0.44)	n.a.	n.a.
O.M. (%)[a]	0.6	3.4	n.a.	n.a.
$CaCO_3$ eq. (%)[a]	15	0.2	n.a.	n.a.
Inorganic C (%)[a]	2.7	0.05	n.a.	n.a.
Cd (mg kg^{-1})[b]	46.3	0.005	0.25	0.32
Co (mg kg^{-1})[b]	92.8	16.8	6	0.26
Cu (mg kg^{-1})[b]	126	365	14	0.55
Ni (mg kg^{-1})[b]	95.5	296	11	0.47
Pb (mg kg^{-1})[b]	2205	29	35	<0.01
Sb (mg kg^{-1})[b]	30.5	0.05	0.05	<0.01
Zn (mg kg^{-1})[b]	657	34	98	15.7

Note: Parenthetic values are standard deviations of the mean, where $n = 3$.

[a] A composite sample was sent to the Laboratory Services Division of the University of Guelph, Guelph, Ontario; results were considered acceptable if the internal reference material measurement fell within three standard deviations of the expected value.

[b] A composite sample was submitted to ALS Laboratory Group, Kitchener, Ontario; results were considered valid if the reference material was recovered within 80%.

function of the final extract pH. The first objective of this paper was to evaluate the efficacy of cement or $Ca(OH)_2$ at reducing trace element mobility, as a function of extraction pH. The second objective was to separate the effect of $Ca(OH)_2$ from cement, from the effect of cement hydration products, on trace element mobility. The third objective was to determine the role of precipitation/dissolution reactions in trace element mobility in cement-treated soils.

2. Materials and methods

The first soil ("SO") was from an old industrial site in southern Ontario, used for 45 years in the production of porcelain enamel frit, ceramic glazes, powder coatings, thermoplastics and gel-coats. Trace element contamination mainly originated from the use of coloured pigments. In 2005, remediation of this site was effected by stockpiling metal-impacted soil on a small portion of the site. The soil was dark to very dark greyish brown sandy loam, and contained about 22% clay and 45% sand. The second soil ("NO") was taken near Sudbury, Ontario where it was contaminated mostly with nickel, copper and cobalt from nearby nickel smelters. It was a dark yellowish brown sandy loam soil from the top 5 cm organic horizon, overlaying non-calcareous silty material. The soil contained 4.5% clay and 55% sand.

Soils were characterized (Table 1). Soil pH was measured with a combined glass electrode (Accumet, AccupHast, Fisher Scientific) using a soil-to-water ratio of 1:2 [15]. Soil electrical conductivity was measured at a fixed soil-to-water ratio of 1:5 [16]. The organic matter (O.M.) content was determined by the Walkley-Black wet oxidation method [17]. Inorganic C was measured with a LECO SC-444 Sulphur and Carbon Analyzer (LECO Corporation, St. Joseph, MI) after ashing the samples at 475 °C. The soil carbonate content equivalent was determined with the HCl method [18]. The cation exchange capacity was determined by the $BaCl_2$ displacement method [19]. Soils were tested for particle-size distribution using the pipette method [20]. Finally, soils were prepared for determination of total available trace element (Cd, Co, Cu, Ni, Pb, Sb and Zn) concentrations by using the HNO_3–H_2O_2 acid digestion method EPA 3050 [21]. The liming agents were also characterized (Table 1). The cement used was ordinary Portland cement (St-Lawrence Cement (now Holcim Canada Inc.), Mississauga, Ontario, Canada). Calcium hydroxide was A.C.S grade (Fisher). Cement and $Ca(OH)_2$ total available trace element (Cd, Co, Cu, Ni, Pb, Sb and Zn) concentrations were determined using the HNO_3–H_2O_2 acid digestion method EPA 3050 [21].

Large bulk quantities of contaminated soil were collected from several places in the stockpiles. After collection, soils were homogenised, sieved to 2 mm and dried at 60 °C in a forced air oven prior to amendment with cement or calcium hydroxide. Soils were amended as follows: dry soil was first homogenised for 2 min with a stainless-steel mixer (KitchenAid brand stand mixer, wire whip blade). After homogenisation, cement or calcium hydroxide was added and mixed again until visual homogeneity. Then water was added, and the soil was mixed again until visual homogeneity, after which it was transferred into a closed 1 L plastic container. The cement-to-soil ratio (c/s) was 0.15 (dry weight of cement/initial dry weight of soil) and the water-to-soil (w/s) was 0.17. A calcium hydroxide-to-soil ratio (ca/s) of 0.0375 (dry weight of calcium hydroxide/initial dry weight of soil) and a w/s of 0.19 was used. The amount of $Ca(OH)_2$ was chosen to match the amount of $Ca(OH)_2$ produced by cement hydration, as found in the literature. $Ca(OH)_2$ is responsible for 90–100% of the pH increase in hydrated cement and constitutes about 25% of the final cement weight [22]. Control soils received neither cement nor $Ca(OH)_2$. Treated soils were cured for 28 days at 22 ± 1 °C in a controlled temperature chamber.

After curing, soils were dried and passed through a 2 mm sieve prior leaching once with diluted HNO_3 solution. The pH of the control soils was adjusted with nitric acid or NaOH. The range of concentrations for leaching was chosen so that there were at least two experimental units per unit of pH between that of the treated soil (pH 11–12.5) and pH 4. Each soil thus had about 15 extracts. The methodology of the extraction was based on the Toxicity Characteristic Leaching Procedure (TCLP) [23]: briefly, soil was extracted with diluted acid (HNO3) for 18 h in a rotary agitation apparatus (during which time the pH would change) with a soil:solution ratio of 1:20. After the extraction, the liquid portion was filtered with 0.22 μm nylon membrane filters (MAGNA) and measured by ICP-OES (Varian Vista Pro) for trace element concentrations. Extract pH was measured with a combined glass electrode (Accumet, AccupHast, Fisher Scientific). The reported pH is the final pH after the extraction, and is considered to be at equilibrium with the extracting solution.

Theoretical solubility of trace elements sulphate, oxide, hydroxide and carbonate precipitate in cement-treated soils was estimated using Visual MINTEQ software, version 2.53, using the solubility constants therein. For $Ca(Sb(OH)_6)_2$, a solubility constant of 2.818×10^{-13} was used [24]. The maximum trace element (and calcium) concentrations in solution were calculated by assuming that the total amount of a trace element present in the soil was a single precipitate (e.g. $Cd(OH)_2$). The carbonate concentration in solution was estimated from the total inorganic carbon soil content [25]. Sulphate, chloride and nitrate in soil extracts were measured according to the EPA ionic chromatography method 300.0 [26].