

## BARIUM LEACHING FROM ALLUVIAL SOILS AND CERTIFIED REFERENCE MATERIALS

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### Introduction

Despite the fact that Ba is the 14<sup>th</sup> most abundant element on Earth, and concentrations in soil are often elevated, relatively few studies deal with the occurrence of Ba in soil. Information on how changing environmental conditions, assessed by laboratory or field investigations, can potentially affect Ba mobility is only scarcely available. Nevertheless, the increased use of barite, for example as a weighting agent for drilling mud in the oil and gas sector, attracted the attention to this element in recent years. Other applications of Ba are its use in superconductors and contrasting agents. In British Columbia, matrix numerical soil standards for Ba were supplemented with an extraction method for the determination of soluble barium (Alberta Environment, 2009). Leaching tests and extractions that have been developed to evaluate heavy metal mobility in soils, ask for a careful interpretation when Ba is considered, and are probably not always suited for Ba because of unintended side effects such as precipitation reactions. In the present study, the release of Ba from soil samples characterized by a varying clay and organic matter content and a wide range of total Ba concentrations, was investigated using commonly applied single and sequential extractions, pH<sub>stat</sub> leaching tests and column tests. Additionally, certified reference materials were analyzed, in order to provide data for Ba, which are not yet available at the moment.

### Methods

Thirteen surface soil samples, taken from different soil types (fluvisols, spolic regosols and histosols) located in the proximity of rivers, were sampled in Flanders (Belgium). Samples were analyzed for their total content of major and trace elements (ICP-MS analysis after sample destruction with concentrated HF, HCl and HNO<sub>3</sub>), organic carbon content, grain size distribution and cation exchange capacity (CEC). pH<sub>stat</sub> leaching tests (at pH 2, 4, 6, 7, 8 and 10) and geochemical modelling. (Visual MINTEQ) were performed on all the samples as described in Cappuyns et al. (2014). During the pH<sub>stat</sub> leaching test, the kinetics of element release was also monitored during 96 h. A column leaching test (NEN7343) was performed on 4 samples, collecting the leachate at liquid/solid (L/S) ratios from 0.1 to 10 L/kg. The influence of higher S/L ratios was investigated with a serial batch test in which the soil material was successively extracted five times with water at a L/S ratio of 20, resulting in L/S ratios from 20 to 100 L/kg. Single extractions with CH<sub>3</sub>COOH (0.43 mol/L) and NH<sub>4</sub>-EDTA (0.05 mol/L) and the BCR sequential extraction were performed according to standardized methods (Rauret et al., 1999; Cappuyns, 2012). Two reference materials (BCR-701 and CRM483) were also analyzed.

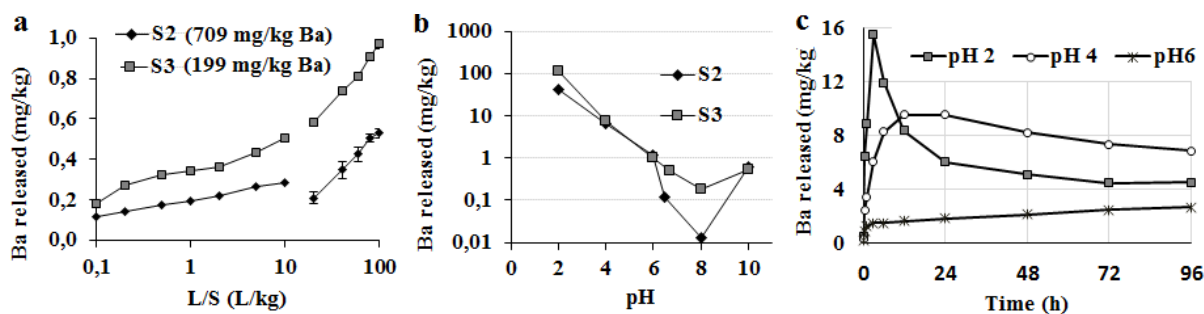
### Results and discussion

Total Ba concentrations in the samples were in the range 179-709 mg/kg (dry matter), pH was around neutral (6.3-7.9), organic carbon content was in the range 2.7-10.4 % and CEC was between 19 and 36 cmol/kg. The BCR sequential extraction was performed on 2 reference materials (Table 1) and on 8 samples with different contents of Fe(hydr)oxides, clay and organic carbon. For the reference materials, the residual fraction ('Step 4') was not determined, since the certification reports do not provide these results for other elements neither. In the more clay-rich samples, Ba was mostly found in the residual fraction, whereas in the samples rich in Fe(hydr)oxides, the 'reducible fraction' (extracted with NH<sub>2</sub>OH.HCl 0.5 M, pH=1.5 ('Step 2')) accounted for more than 50% of the total Ba content.

**Table 1.** Amount of Ba (in mg/kg) extracted from two certified reference materials (CRM 483 and BCR 701) in the first 3 steps of the BCR sequential extraction procedure. Average  $\pm$  standard deviation of 4 replicates.

	Step 1	Step 2	Step 3
	CH <sub>3</sub> COOH 0.11 mol/L	NH <sub>2</sub> OH.HCl 0.5 mol/L	H <sub>2</sub> O <sub>2</sub> 8.8 mol/L
CRM 483	8,1 $\pm$ 0,16	300 $\pm$ 5,0	48 $\pm$ 0,86
BCR 701	17,9 $\pm$ 0,13	97 $\pm$ 1,4	13 $\pm$ 0,17

The amount of Ba extracted with CH<sub>3</sub>COOH 0.43 mol/L (L/S = 10 L/kg) was slightly higher than the amount of Ba released in the first step of the BCR sequential extraction procedure (CH<sub>3</sub>COOH 0.11 mol/L, L/S = 40 L/kg). NH<sub>4</sub>-EDTA showed a low capacity to extract Ba, as on average less than 3 % of the total Ba content could be extracted with NH<sub>4</sub>-EDTA. **In the column and serial batch leaching test, the pH of the leachate was around neutral, and the cumulative release of Ba was less than 1 mg/kg, even in the sample with the highest total Ba content (S2) (Figure 1a). Barium was most significantly released at acid pH values (Figure 1b). At pH 2 and 4, (Figure 1c) Ba leaching is characterized by a maximum after resp. 3 and 12h, after which concentrations decrease exponentially, most likely due to the precipitation of Ba.**

**Figure 1.** (a) Cumulative release of Ba as a function of L/S ratio from sample S1 during the column test (L/S= 0.1-10) and the serial batch test (L/S = 20-100 L/kg); (b) Release of Ba from samples S2 and S3 as a function of pH after 96 h of pH<sub>stat</sub> leaching (c); Release of Ba as a function of time during pH<sub>stat</sub> leaching (sample S1, 389 mg/kg Ba)

## Conclusion

Despite relatively high total concentrations in soil, Ba showed a low mobility in the alluvial soils investigated in the present study, indicating that only a very small proportion of Ba is readily available for uptake by plants or for leaching. Acidification of the soils (below pH 4) can cause a substantial release of Ba. The investigation of leaching of Ba as a function of time, and geochemical modelling showed that, during leaching tests, unintended side-effects, such as precipitation of BaSO<sub>4</sub> can influence the results.

## References

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