

# **Mobilization Mechanisms of Soluble and Dispersible Heavy Metals and Metalloids in Soils**

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Dedicated to my parents



*Ich höre und vergesse,  
ich sehe und behalte,  
ich handle und verstehe.*

*(alte konfuzianische Weisheit)*



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# List of Abbreviations

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B: Buch soil

COC: colloidal organic carbon

DCM: Dichlormethane

DOC: dissolved organic carbon

DOM: dissolved organic matter

FFF: field-flow fractionation

FNU: Formazin nephelometric unit (unit of turbidity)

GS: Gütersloh soil

MED: Molarity of Ethanol droplet

MTUF: Multi-stage tangential ultrafiltration

OM: organic matter

TG: Tiergarten soil

TOC: total organic carbon

WDPT: Water droplet penetration time

# Abstract

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Colloidal heavy metals are known to be easily translocatable along preferential flow paths in soils and therefore pose a significant risk of groundwater pollution. To estimate potential leaching of metals from contaminated sites not only in dissolved but also in colloidal form an understanding of underlying mechanisms governing dispersible metal mobilization is crucial. In addition the knowledge of colloid composition is important. The presented thesis investigates these physico-chemical mechanisms of soluble and dispersible metal mobilization in two examples, namely (1) the impact of drying and rewetting of soils on the mobilization of soluble and dispersible Cd, Cu, Pb, and Zn and (2) the impact of soil liming on the mobilization of soluble and dispersible Pb, As, and Sb. The quality of colloids was considered in particular.

I tested the hypothesis that 1) drying of soil samples increases not only the hydrophobicity of the solid phase but also the hydrophobicity of the dispersed colloids and that 2) drying of soil samples leads to an increase in colloidal and dissolved metal concentrations. In the context of liming, I tested the hypothesis that 3) the pH-induced increase in particle charge leads to a greater dispersion of colloids with increasing pH and thus increases colloidal Pb, As and Sb. Furthermore I hypothesized that 4) the addition of  $\text{Ca}^{2+}$  reduces this pH effect by enhancing colloid flocculation. In addition, I tested the assumption that 5) both a change in pH and counterion valency impact on the quality and size distribution of colloids. I investigated 6) the influence of a pH increase on the mobilization of soluble and dispersible Pb, As, and Sb in a polluted organic-rich soil and tested the hypothesis that 7) divalent cations attenuate the pH effect by a) “neutralizing” negative colloid charge and by b) immobilizing dissolved As and Sb by the formation of inorganic precipitates. Before I could test my hypotheses the development of methods to characterize colloid properties was essential: The C18-method determines the hydrophobicity of dispersed colloids and the development of a multi-stage tangential ultrafiltration (MTUF) method serves the characterization of the separated colloids and associated metal(loid)s in soil suspensions. In addition, I developed an approach to estimate the percentage of dispersed organic-dominated and mineral-dominated colloids by combining results gained by MTUF and centrifugation. I tested all hypotheses on filtered aqueous extracts (1.2  $\mu\text{m}$ ) of batch experiments.

To test hypotheses 1 and 2 I determined turbidity, zeta potential, hydrophobicity and size of dispersed colloids of field-moist and air-dried topsoil samples of a former sewage farm. I measured dissolved and colloidal concentrations of heavy metals and organic C in the suspensions and determined the hydrophobicity of the soil solid phase.

Whereas drying of soil led to an increase in hydrophobicity of the solid phase, it did not increase the hydrophobicity of dispersed colloids. Drying led to the mobilization of organic colloids, but immobilized (organo-)mineral colloids. While concentrations of the investigated dissolved heavy metals increased

in all soil samples, concentrations of colloidal heavy metals decreased in almost all soil samples for Cd and Zn, in some soils for Cu and Pb.

I conducted the experiments related to liming with topsoil samples from former shooting ranges and increased the pH of the batch samples by adding dilute solutions of either a monovalent (KOH) or a divalent  $\text{Ca}(\text{OH})_2$  base. I used an organic-rich soil ( $C_{\text{org}}$ : 21 %) to test hypotheses 3 and 4. Hypotheses 3 – 5 were tested on a soil with a low C/Fe-ratio ( $C_{\text{org}}$ : 9 %) while experiments related to 6 and 7 were conducted on a soil with a high C/Fe-ratio ( $C_{\text{org}}$ : 8 %). Soil colloid fractionation was done using the developed MTUF (hypothesis 5). In the suspensions, I measured zeta potential, particle size, turbidity and dissolved and colloidal concentrations of Pb, As, Sb, Fe, and organic C. Results of the organic-rich soil showed that colloids may be stabilized by charge and by steric effects. The combination of both effects renders dispersed organic colloids at pH 4 much more stable than colloids dispersed from soils with less organic C. While concentrations of colloidal Pb increased continuously in the presence of KOH, they only increased at pH > 5.8 in the presence of  $\text{Ca}(\text{OH})_2$  due to charge compensation of the negatively charged colloids by the divalent Ca cation. Colloid characterization by MTUF showed that the valency of the counterion controls quantity, elemental composition and size of the colloids. Increasing the pH using KOH led to the dispersion of sesquioxides and organic colloids (9 nm – 220 nm). Colloidal As and Pb were found to be associated with sesquioxides which may in part be stabilized by organic C. Increasing the pH using  $\text{Ca}(\text{OH})_2$  suppressed the dispersion of sesquioxides and induced the formation of larger colloids (0.22 – 1.2  $\mu\text{m}$ ) such as precipitation products of Pb and “bridging”-products of Ca and DOM, which may also include some Pb. While my data of the high C/Fe-soil excludes the formation of inorganic precipitates it suggests that the counterion valency controls the mobility of the sorbents (i.e. colloids, DOM) and the sorption capacity of the sorbents. A liming-induced pH increase does not pose any major risk of dispersible As and Sb mobilization as long as divalent cations dominate in solution. However, the mobilization of soluble Sb needs to be considered.

My results showed that different mechanisms are responsible for the mobilization of soluble and dispersible metal(loid)s in both a liming-induced pH increase as well as in a drying event. My data suggest that the composition of the soil solid phase, i.e.  $C_{\text{org}}$  and sesquioxide content, may control colloid release and the distribution of the respective metal between soluble and colloidal phases. Future studies should investigate more soils across a wider range of composition in order to gain a better understanding about the role of the composition of the soil sorbents not only in soluble but also in dispersible metal(loid) mobilization. In addition, field experiments should clarify the relevance of the identified mechanisms to colloidal metal leaching.

# Zusammenfassung

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Kolloidale Schwermetalle sind dafür bekannt, dass sie entlang präferentieller Fließwege im Boden leicht verlagerbar sind. Daher stellen sie ein bedeutendes Risiko für die Verschmutzung des Grundwassers dar. Für die Abschätzung möglicher Schwermetallauswaschungen an kontaminierten Standorten - nicht nur in gelöster sondern auch in kolloidaler Form - ist ein Verständnis der Mobilisierungsmechanismen löslicher sowie dispergierbarer Metallionen unabdingbar. Darüber hinaus sind Kenntnisse über die Zusammensetzung der Kolloide wichtig. Gegenstand der vorgelegten Doktorarbeit ist die Untersuchung dieser physiko-chemischen Mobilisierungsmechanismen löslicher und dispergierbarer Metalle anhand zweier Beispielfälle: (1) Einfluss einer Trocknung und Wiederbefeuchtung von Böden auf die Mobilisierung von löslichem und dispergierbarem Cd, Cu, Pb und Zn sowie (2) Einfluss einer Bodenkalkung auf die Mobilisierung von löslichem und dispergierbarem Pb, As und Sb unter besonderer Berücksichtigung der Kolloidzusammensetzung.

Ich überprüfte die Frage, ob 1) Trocknung von Bodenproben nicht nur die Hydrophobizität der Festphase, sondern auch die der dispergierten Kolloide erhöht und 2) ob Trocknung von Bodenproben zu einer Erhöhung der gelösten und kolloidalen Metallkonzentrationen führt. Im Zusammenhang einer Kalkung überprüfte ich die Frage, ob 3) bei steigendem pH-Wert die dadurch induzierte Erhöhung der Partikelladung zu einer stärkeren Dispergierung von Kolloiden führt und es deshalb zu einer Zunahme an kolloidalem Pb, As und Sb kommt. Darüber hinaus nahm ich an, dass 4) die Zugabe von  $\text{Ca}^{2+}$  die Wirkung des pH-Wertes durch Begünstigung von Kolloidflockung verringert. Zusätzlich überprüfte ich die Annahme, dass 5) sowohl eine Änderung des pH-Wertes als auch der Valenz der Gegenionen die Qualität und die Größenverteilung der Kolloide beeinflussen. Ich untersuchte 6) den Einfluss eines pH-Anstieges auf die Mobilisierung von löslichem und dispergierbarem Pb, As und Sb in einem kontaminierten Boden, der reich an organischer Substanz ist. Dabei überprüfte ich die Frage, ob 7) zweiwertige Kationen die Wirkung des pH-Wertes abschwächen durch a) ein „Neutralisieren“ der negativen Kolloidladung und durch b) Immobilisierung gelösten As und Sb durch die Bildung anorganischer Präzipitate. Ein wesentlicher Aspekt der Arbeit war dabei die Entwicklung von Methoden zur Kolloidcharakterisierung: Die C-18-Methode erlaubt die Bestimmung der Hydrophobizität von Kolloiden und multi-stage tangential Ultrafiltration (MTUF) gestattet die Charakterisierung aufgetrennter Kolloide und daran assoziierter (Halb-)Metalle in Bodensuspensionen. Zusätzlich entwickelte ich einen Ansatz, der durch eine Kombination von Ergebnissen aus MTUF und Zentrifugation die Abschätzung des Prozentsatzes an dispergierten organisch- und mineralisch-dominierten Kolloiden ermöglicht. Alle Fragen wurden an gefilterten wässrigen Extrakten (1.2  $\mu\text{m}$ ) von Schüttelversuchen überprüft.

Um die Fragen 1 und 2 zu überprüfen bestimmte ich Trübe, Zetapotential, Hydrophobizität und Größe der dispergierten Kolloide feldfrischer und luftgetrockneter Böden eines Rieselfeldes. Ich maß gelöste

und kolloidale Konzentrationen an Schwermetallen und organischem C in den Suspensionen und bestimmte die Hydrophobizität der Bodenfestphase.

Während Trocknung zu einem Anstieg der Hydrophobizität der Festphase führte, erhöhte sich die Hydrophobizität der dispergierten Kolloide nicht. Trocknung mobilisierte organische Kolloide, aber immobilisierte (organo-)mineralische Kolloide. Die Konzentrationen an kolloidalen Schwermetallen nahm bezüglich Cd und Zn in fast allen Böden und bezüglich Cu und Pb in einigen Böden ab, wohingegen die Konzentrationen an den untersuchten gelösten Schwermetallen anstieg.

Die auf die Kalkung bezogenen Versuche führte ich mit Oberbodenproben von Schießplätzen durch und erhöhte dabei den pH-Wert der Schüttelproben durch die Zugabe von verdünnten Lösungen einer einwertigen (KOH) oder zweiwertigen ( $\text{Ca}(\text{OH})_2$ ) Base. Die Fragen 3 und 4 untersuchte ich an einem an organischer Substanz reichen Boden ( $C_{\text{org}}$ : 21 %). Die Fragen 3 bis 5 wurden an einem Boden mit einem niedrigen C/Fe-Verhältnis ( $C_{\text{org}}$ : 9 %) überprüft, während auf Frage 6 und 7 bezogene Versuche an einem Boden mit einem hohen C/Fe-Verhältnis ( $C_{\text{org}}$ : 8 %) durchgeführt wurden. Die zur Überprüfung von Frage 5 erforderliche Fraktionierung der Bodenkolloide erfolgte durch die entwickelte MTUF-Methode. In den Suspensionen bestimmte ich Zetapotential, Partikelgröße, Trübung sowie gelöste und kolloidale Konzentrationen an Pb, As, Sb, Fe und organischem C.

Die Ergebnisse des an organischer Substanz reichen Bodens zeigten, dass Kolloide aufgrund ihrer Ladung als auch durch sterische Effekte stabilisiert werden. Die Kombination beider Effekte stabilisiert dispergierte organische Kolloide bei pH 4 weitaus besser als Kolloide, die weniger C enthalten. Während in der Anwesenheit von KOH die Konzentrationen an kolloidalem Pb kontinuierlich anstiegen, erhöhten sie sich in Anwesenheit von  $\text{Ca}(\text{OH})_2$  erst bei pH-Werten  $> 5,8$ . Letzteres ist auf eine Kompensation der negativen Kolloidladung durch das zweiwertige Ca-Kation zurückzuführen. Die Charakterisierung der Kolloide mittels MTUF zeigte, dass die Valenz der Gegenionen die Menge, die elementare Zusammensetzung als auch die Größe der Kolloide steuert. Eine pH-Erhöhung durch KOH führte zur Dispergierung von Sesquioxiden und organischen Kolloiden (9 nm – 220 nm). Kolloidales As und Pb sind dabei mit Sesquioxiden assoziiert, die teilweise durch organischen C stabilisiert sein können. Eine pH-Erhöhung durch  $\text{Ca}(\text{OH})_2$  unterdrückte die Dispergierung der Sesquioxide und induzierte die Bildung von größeren Kolloiden (0,22 – 1,2  $\mu\text{m}$ ) wie Fällungsprodukte von Pb und „Brückenbindungsprodukte“ von Ca und DOM, die auch Pb enthalten können. Während die Daten des Bodens mit dem hohen C/Fe-Verhältnisse die Bildung anorganischer Präzipitate ausschließen, deuten sie darauf hin, dass die Valenz der Gegenionen die Mobilität der Sorbenten (d. h. Kolloide und DOM) als auch die Sorptionskapazität der Sorbenten steuert. Ein kalkungsinduzierter pH-Anstieg stellt kein Risiko für die Mobilisierung dispergierbaren As und Sb dar, so lange zweiwertige Kationen die Lösung dominieren. Allerdings darf die Mobilisierung von löslichem Sb nicht außer Acht gelassen werden.

Meine Ergebnisse zeigen, dass unterschiedliche Mechanismen für die Mobilisierung von löslichen und dispergierbaren (Halb-)Metallen bei einem kalkungsinduzierten pH-Anstieg als auch bei einer

Trocknung verantwortlich sind. Sie weisen darauf hin, dass die Zusammensetzung der Bodenfestphase, d. h. der  $C_{org}$ - und Sesquioxidgehalt, die Kolloidfreisetzung als auch die Verteilung des jeweiligen (Halb-)Metalls zwischen gelöster und kolloidaler Phase steuern kann. Zukünftige Studien sollten mehr Böden über eine breitere Zusammensetzung hinweg untersuchen, um ein besseres Verständnis über die Rolle der Zusammensetzung der Bodensorbenten - nicht nur bei der Mobilisierung von löslichen sondern auch von dispergierbaren (Halb-)Metallen - zu erlangen. Ergänzend sollten Feldversuche die Relevanz der identifizierten Mechanismen zur Auswaschung kolloidaler Metalle klären.

# 1 General Introduction

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Heavy metal contamination of soil through both anthropogenic and natural sources has occurred throughout the world and has been recognized as a global problem. It may pose a significant risk to human (Mani and Kumar, 2005) and environmental health through e.g. groundwater pollution (Sorvari et al., 2006) and toxicosis of wildlife (Lewis et al., 2001). Sewage farms (Blume et al., 1980) and shooting ranges (Neite et al., 1999) are examples for sites severely contaminated by heavy metals. According to Herms and Brümmer (1984) the ecological relevance of heavy metals in soils is mainly controlled by their soluble and labile pools, representing those fractions which are easily bioavailable and translocatable. Therefore, solubility and bioavailability of heavy metals have become the main focus of many environmental studies. While these studies commonly investigated dissolved metal fractions (generally defined as  $< 0.45 \mu\text{m}$ ) only (for instance Tack et al., 1999) recently published results have shown that a significant fraction of conventionally defined dissolved fractions is actually existent in colloidal form (Douglas et al., 1993; Sanudo-Wilhelmy et al., 1996; Lyvén et al., 2003), which McCarthy and Zachara (1989) describe – beside the solid and dissolved phase – as a third phase in the subsurface environment. The association of heavy metals and metalloids with mobilized colloids is controlled by the affinity of the respective metal to the colloids (Pourret et al., 2007), the properties of colloids (Lyvén et al., 2003) and soil solution. The distribution of a metal between these phases will determine its fate and transport in the environment (Hassellöv et al., 1999).

Due to their small size (Brezesinski and Mögel 1993; Pourret et al., 2007) and their large surface to volume ratio (Kretzschmar et al., 1999) colloids tend to be stable in suspensions. As a result, colloids are hardly filtered by porous media (i. e. physically and physico-chemically) if they travel through preferential flow paths (Seta and Karathanasis, 1997). Unlike truly dissolved metals colloid-associated metals may therefore easily be translocated into deeper parts of the soil and groundwater. Several authors (Denaix et al., 2001; Jensen et al., 1999) even say that colloids facilitate the subsurface transport and mobilization of heavy metals at contaminated

sites. Failure to consider this pathway may thus result in an underestimation of not only distances which contaminants may possibly migrate but also of the amount of contaminants which is being translocated with the water flow (McCarthy and Zachara, 1989). The different behaviour of “truly” dissolved and colloid-associated heavy metals in soil and aquatic environments requires a differentiation between these two forms of metals in order to gain a realistic understanding about potential metal release, spatial distribution, bioavailability and the ultimate impact on human health.

To understand the relevance of colloidal metal mobilization to potential metal leaching on contaminated sites the knowledge of the underlying mechanism is crucial. With respect to the binding of metals to colloids the properties of colloids are of vital importance. Prevailing environmental conditions, on the other hand, may control the mechanisms which govern colloid release and stability.

### **1.1 Soil colloid characteristics, characterization and mobilization**

Colloids are characterized by properties such as composition, surface charge, surface area, size and shape (Ranville et al., 1999). These parameters govern colloid interactions with pollutants as well as colloid mobilization and stability.

#### ***1.1.1 The role of colloid composition and size in metal binding to colloids***

Colloid composition determines – together with physico-chemical parameters of the soil solution such as pH and ionic strength – the surface charge. Brady and Weil (2002) describe colloid surface charge to be responsible for the sorption of heavy metals. Several studies underline the relevance of colloid composition in order to estimate the fate and bioavailability of associated elements. Pourret et al. (2007) differentiate between an organic and inorganic colloidal pool. The authors found that individual metals are partitioned in these two colloidal pools. An important role was attributed to colloidal organic matter since a large fraction of trace metals was found to be associated with it (Tanizaki et al., 1992; Dupré et al., 1999). Similarly, Lyvén et al. (2003) report Fe- and organic C-based colloids to be the most important potential carriers for other elements. Not only differ both types of colloidal carriers in their size

distribution but also in their trace metal content. They conclude metals to have varying affinities to these different types of colloidal pools. Colloid composition, together with the type of bonding the metal is linked to the colloid, control trace element geochemical cycles or their fate in the environment (Pourret et al., 2007).

Kretzschmar et al. (1999) describe the particle size as one of the most important characteristics of mobile colloids since they determine the specific surface area of colloidal particles, which controls the degree of contaminant sorption. The size fractionation of soil colloids together with the characterization of their elemental composition may thus provide important information for a better understanding and prediction of their role as carriers of different pollutants (Buffle and Leppard, 1995). Therefore, the use of powerful methods for suspended soil colloid fractionation is crucial. Since the stability of suspended soil colloids is very much subject to changes in ionic strength, separation techniques which cause little disturbance of sample equilibrium are an indispensable prerequisite for a successful fractionation. This prerequisite is met by common fractionation techniques such as ultrafiltration and centrifugation (Nifant'eva et al., 2001), which are considered a powerful tool for the investigation of colloidal particles in natural environments (Kretzschmar et al., 1999).

While the investigation of colloid composition with respect to the bindings of metals has already gained some attention there are no studies focusing on colloid composition in the context of colloid mobilization.

### ***1.1.2 Colloid mobilization in soils***

Colloid charge is known to be a key parameter for colloid stability (Séguaris and Lewandowski, 2003). In addition, size and shape are other important factors controlling colloid transport and deposition in soil (Ranville et al., 1999). Therefore, colloid properties such as charge and size play an important role in colloid mobilization. In order to estimate potential leaching of metals from contaminated sites not only in dissolved but also in colloidal form the knowledge of underlying mechanisms governing colloidal metal mobilization is crucial. Colloid mobilization is controlled by physical factors such as shear forces (Kaplan et al., 1993; Rousseau et

al., 2004) as well as (physico)-chemical parameters of the soil solid (Kretzschmar et al., 1993) and solution phase (Kaplan et al., 1996). However, the dominating mechanisms may vary for different environmental conditions. The presented thesis investigates these physico-chemical mechanisms of colloidal metal mobilization in two exemplary scenarios, namely (1) drying and rewetting of soils and (2) liming of soil in the context of soil stabilization and remediation. Both, drying as well as liming, are known to be conducive to the potential mobilization of colloid-associated heavy metals.

### **1.2 Mobilization of soluble and colloidal metals in soils**

#### ***1.2.1 The impact of drying on the mobilization of soluble and colloidal metals***

Under natural conditions almost any soil is subject to wetting and drying cycles. Drying may alter the physico-chemical properties of the soil such as conformation of soil organic matter (Hurraß and Schaumann, 2006) and hydrophobicity (Dörr et al., 2000; Dekker et al., 2001). Upon rewetting, these changed physico-chemical properties of the soil may affect the composition of the soil solution, which is reflected – amongst others – in increasing dissolved concentrations of organic carbon and dissolved heavy metals (Wang et al., 2002; Tom-Petersen et al., 2004).

However, at the moment there is only little knowledge about the impact of wetting and drying cycles on the physico-chemical properties of colloids. Wan and Wilson (1994a) suggest colloid hydrophobicity to be an important parameter controlling colloid retention in soil. The authors observed an increasing retention of colloidal latex particles and bacteria with increasing particle hydrophobicity. Furthermore, Schaumann et al. (2002) reported that the state of moisture of soil samples containing organic matter affects colloidal characteristics of aqueous soil extracts. The authors found increasing colloid particle sizes and decreasing molecular sizes of humic associates following drying. These drying-induced changes of physico-chemical properties may alter transport parameters of both colloidal and dissolved phase. Therefore, the understanding of possible differences in colloid mobilization and associated heavy metals from dried and field-moist samples together with the

underlying mechanism is essential not only for the design of batch and column experiments but also for the risk assessment of contaminated sites.

### ***1.2.2 The impact of liming on the mobilization of soluble and colloidal metal(loid)s***

Liming is a common method suggested for soil remediation and stabilization of shooting range soils (EPA, 2001). Whilst drying as a physical impact factor affects soil solution chemistry indirectly, the application of lime onto the soil directly affects the chemical properties of the soil solution as well as the solid phase. The induced pH-increase of the soil solution is meant to immobilize or precipitate heavy metals in soils (Lindsay, 1979). However, the increase in pH as well as the possibly resulting mobilization of dissolved organic matter may promote the mobilization of colloids (Kretzschmar et al., 1993; Kaplan et al., 1996). On the other hand, the addition of Ca ions into the soil leads to a compression of the diffusive double layer (McBride, 1994) facilitating colloid flocculation. While both processes have been studied individually in depth (Kretzschmar et al., 1993), their net effect on colloid mobilization is yet unclear.

The metals of main concern on shooting range soils are Pb, As and Sb. While the relevance of colloidal Pb (Denaix et al., 2001; Jensen et al., 1999) and the impact of liming on the mobilization of soluble Pb is well documented (Turpeinen et al., 2000), studies on the pH-induced mobilization of colloidal Pb are missing.

Since numerous publications report increasing dissolved As concentrations with increasing pH (for instance Tyler and Olsson, 2001; Xu et al., 1988) significant effects of lime application are to be expected. However, there is only little knowledge about As in association with colloids. Slowey et al. (2007) found As(V) sorbed to poorly crystalline Fe(III)-hydroxides and Tanizaki et al. (1992) demonstrated As not only to be present as simple ion but also associated with small ( $10^4$  - 500 Da) inorganic colloids. Similarly, Slowey et al. (2007) reported the occurrence of As on colloids < 20 nm and ~ 100 nm.

Similar to As, up to now, there is only little evidence of the occurrence of colloidal Sb. Buddemeier and Hunt (1988) found  $^{125}\text{Sb}$  to be associated with colloids of a size range between 3 and 50 nm and Lyvén et al. (2003) report Sb linked with organic carbon colloids. Since Sb is reported to be strongly sorbed to Fe-oxides at pH-values < 6.5 (Tighe et al. 2005; Edwards et al., 1999) colloid-associated Sb might become relevant in a liming induced-pH increase.

### **1. 2 Objectives of this thesis**

This thesis aims to elucidate the mobilization of soluble and colloidal metal(loid)s under the influence of two different environmental factors. It investigates the underlying mechanisms and characterizes colloid properties and composition using batch experiments by focusing on the following two aspects:

- 1) Impact of drying on the amount and properties of colloids dispersed as well as the mobilization of soluble and colloid-associated heavy metals (Pb, Cd, Cu, Zn) on a sewage farm at Berlin-Buch.
- 2) Impact of liming on the mobilization of soluble and colloid-associated Pb, As and Sb in soils from former shooting range sites.

In order to better understand the role of hydrophobicity and the composition of the mobilized colloids, the development of appropriate methods was essential. The development of a method for the determination of hydrophobicity of suspended soil colloids is described in chapter 2. The development of a multi-stage tangential ultrafiltration (MTUF) method, which lives up to the requirements of the separation of colloids in soil suspension, served the characterization of the separated colloids together with associated metal(loid)s. The application of MTUF is meant to elucidate the role of differently composed colloids in metal(loid) mobilization. Furthermore, it demonstrates that a combination of results gained by MTUF and centrifugation may be drawn on in order to provide an estimate for (a) colloids mainly composed of mineral and (b) colloids predominantly consisting of organic matter. The results of this study are shown in chapter 5.

*Chapter 2* describes the development of a method using C18 column material which serves the determination of hydrophobicity of suspended soil colloids. This method provides the basis for the following study of the underlying mechanism of colloids released after drying.

In *chapter 3* I investigated whether (a) drying of soil samples increases not only the hydrophobicity of the solid phase but also the hydrophobicity of the dispersed colloids and whether (b) drying of soil samples increases the colloid-bound and dissolved metal fractions.

*Chapter 4* is dedicated to the study of the effect of pH and the role of counterion valency on the mobilization of soluble and colloidal Pb. In addition, it elucidates the mechanisms which control colloid release as a function of pH and counterion valency. In the context of liming, I tested the hypothesis that the pH-induced increase in particle charge leads to a greater dispersion of colloids with increasing pH and thus increases mobilization of colloidal Pb. Furthermore, I hypothesized that the addition of  $\text{Ca}^{2+}$  counteracts the pH effect, thus resulting in lower colloidal Pb concentrations.

*Chapter 5* introduces the developed design of a multi-stage tangential ultrafiltration system suitable for the fractionation of suspended soil colloids. It compares results obtained by MTUF and centrifugation and demonstrates how a combination of both results allows for an estimate of colloids dominated by organic and mineral material. Furthermore, I hypothesized that increasing pH leads to an increased mobilization of colloidal Pb, As and Sb and that the addition of  $\text{Ca}^{2+}$  reduces this pH-effect. In addition, I tested the assumption that both a change in pH and counterion valency impact on the quality and size distribution of colloids. These hypotheses were tested on a soil with a low C/Fe-ratio.

*Chapter 6* investigates the influence of a pH-increase on the mobilization of soluble and colloidal Pb, As, and Sb in a polluted organic-rich soil (i. e. a soil with a high C/Fe-ratio). I tested the hypothesis whether divalent cations attenuate the pH-effect

by a) “neutralizing” negative colloid charge and b) immobilizing dissolved As and Sb by the formation of inorganic precipitates.

The mobilization of heavy metals and metalloids is the subject of the following chapters. In order to distinguish between the different forms of mobilized metals they are denoted “dissolved” and “colloidal”.

## 2 A Method for the Determination of Hydrophobicity of suspended Soil Colloids

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### **2.1 Abstract**

Colloids play a crucial role in the translocation of trace elements in soils. Recent studies provided hints that colloid hydrophobicity may be an important factor controlling colloid (im)mobilization in soils. However, existing methods for the determination of hydrophobicity are limited to the bulk soil. Therefore, we developed a method to determine the hydrophobicity of suspended colloids in aqueous soil suspensions, which was based on a distribution between a polar and a non-polar phase. The proposed method uses 30 mg of an unpolar solid phase (C18-column material) which are mixed with 10 mL of suspension for 2 hours. The turbidity of the suspensions is measured before and after mixing. The ratio of the colloids in the hydrophilic aqueous and the hydrophobic solid phase is calculated as a measure of colloid hydrophobicity. This method was successfully tested on differently hydrophobized goethite particles. At DOC concentrations exceeding 20 mg l<sup>-1</sup>, organic molecules sorbed to C18-material limit the applicability of the method.

## 2.2 Introduction

Colloids play a crucial role in the translocation of heavy metals (Keller and Domergue, 1996; Jensen et al., 1999; Denaix et al., 2001) and organic contaminants (Brown and Peake, 2003; Bergendahl, 2005; Totsche et al. 2006) in soils. Their mobilization and stability in soils is controlled by physico-chemical factors such as pH, ionic strength and DOM concentration in the soil solution, as well as steric effects (Dekker et al., 2001). Furthermore, there are hints in the literature that hydrophobicity is another important factor controlling colloid retention, stability and sorption capacity. Wan and Wilson (1994a) demonstrated an increased retention of colloidal latex particles and bacteria with increasing particle hydrophobicity in an unsaturated sand column experiment. Similarly, under saturated conditions hydrophobic colloids showed a lower recovery than hydrophilic colloids, allowing the authors to conclude hydrophilic colloids are more mobile than hydrophobic ones (Wan and Wilson, 1994a) as they sorb less strongly to both the gas-water and solid-water interfaces. Breiner et al. (2006) reported hydrophobic organic molecules affect colloid stability in aqueous solutions by altering the surface properties of colloids. They postulate an enhanced hydrophobic nature of the colloids would reduce their transport in the environment. Another parameter hydrophobicity has an effect on is the sorption capacity of colloids. According to Liu and Lee (2006) hydrophobicity is thought to enhance the sorption capacity of colloids for hydrophobic organic compounds. Breiner et al. (2006) suggest organic matter-coated inorganic colloids facilitate the sorption of hydrophobic organic contaminants. Different conditions are reported to induce hydrophobicity, for instance drying, this being explained by changes in the molecular conformation of the organic matter (Liu and Lee, 2006; Ma'shum and Farmer, 1985). In addition, McHale et al. (2005) found wax coatings arising from vegetation to render the surface of small soil particles hydrophobic.

Hydrophobicity is inversely correlated with the wettability of water (Doerr et al., 2000). For pure mineral colloids the surface charge is closely related to the hydrophobicity of colloids. In contrast, organo-mineral colloids of similar surface charge may vary strongly in hydrophobicity, depending on the accessibility of functional groups to surrounding water. For these colloids, hydrophobicity might be a

more suitable indicator for the estimation of sorption capacity and mobility than surface charge.

There are a number of methods for determining the hydrophobicity of the soil solid phase such as the water droplet penetration time test (WDPT; Doerr et al., 2000; Letey, 1969), the Wilhelmy plate method as described by Bachmann et al. (2003) and the molarity of ethanol droplet (MED) test (Roy and McGill, 2002). All these methods, however, can not be applied to dispersed colloids in soil suspensions. Recently, Guiné et al. (2003) proposed a method to determine the hydrophobicity of colloidal bacteria in aqueous suspensions using hexadecane as an extracting solvent. We adopted this approach to colloidal soil suspensions (1:10 water extracts) in a preliminary experiment (unpublished data) but results indicated that this method can not be used for colloidal soil suspensions due to incomplete separation of the aqueous phase and the organic solvent. This incomplete separation may be attributed to the presence of surface-active substances in the soil suspension (such as dissolved organic matter), which cause an emulsion, rendering a complete phase separation impossible. Therefore, the aim of this paper is to discuss a newly developed method for the determination of the hydrophobicity of suspended soil colloids in soil extracts.

## **2.3 Material and Methods**

The two tested methods described in the following are based on a distribution of suspended hydrophobic goethite particles between (a) two liquid phases (Dichlormethane-method) and (b) a hydrophobic solid phase (C18-method).

### ***2.3.1 Approach for method testing***

In view of the findings from van Oss and Giese (1995) that interfacial interactions control hydrophobicity we based the suitability test of the methods described in the following sections on the assumption that there exists a relationship between hydrophobicity and the surface charge of the mineral particle. That is: the higher the charge of the particle, the higher the tendency to remain in suspension. The closer

the particle charge to zero, the worse the hydration process and the higher the tendency to “escape” from water, i. e. attraction by an unpolar phase increases. Hence, if the methods tested proved successful, the resulting hydrophobicity values should increase with decreasing amount of the zeta potential of the colloids.

We applied the methods to differently treated goethite particles in aqueous suspensions. 50 mg goethite was suspended in water, using ultrasonic treatment for 30 min followed by the addition of appropriate quantities of stock solutions [ $\text{NaH}_2\text{PO}_4$  ( $c(\text{PO}_4) = 3800 \text{ mg L}^{-1}$ ),  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$  ( $c(\text{Mg}, \text{Al}) = 1000 \text{ mg L}^{-1}$ )]. The volume was made up to 1 L using deionised water. Final concentrations of the individual solutions were  $c(\text{PO}_4) = c(\text{Al}) = 80 \text{ }\mu\text{M}$ ,  $c(\text{Mg}) = 120 \text{ }\mu\text{M}$ . For the Na treatment, goethite was “washed” in diluted NaOH solution ( $c = 1 \text{ }\mu\text{M}$ ) before being suspended in water. The mixtures were allowed to equilibrate for 16 hours whilst shaking. Aliquots of all suspensions were adjusted to pH 2 – 8 using NaOH and  $\text{HNO}_3$  ( $c = 0.1 \text{ M}$ ) and the zeta potential of the colloids was determined (Zetasizer 2000, Malvern) after completed equilibration.

The goethite was synthesized by ageing of ferrihydrite, which precipitated after mixing  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and KOH solutions at a molar Fe/OH ratio of 0.05 (Schwertmann and Cornell, 1991). For a detailed description see Mikutta et al. (2006).

### **2.3.2 Hydrophobic phases tested for the separation of hydrophobic colloids**

#### **2.3.2.1 Dichlormethane-Method**

Dichlormethane (DCM) has a higher specific weight and a higher polarity than hexadecane (as used by Guiné et al., 2003), allowing for a better phase separation. 3 mL of DCM were added to 12 mL of suspension of each pH-level, in which the turbidity had been determined. The mixture was vortexed for 1 min (level 6) and left to stand for 30 min to allow for phase separation. The aqueous phase was subsequently transferred into the cuvette for turbidity measurement (T2; 2100P ISO Turbidimeter, Hach). Hydrophobicity was calculated according to equation (2.1) in section 2.3.3. Samples of each pH-level were set up in triplicate.

### 2.3.2.2 C18-Method

This separation method used a hydrophobic solid phase (C18 microparticles: 40  $\mu\text{m}$  diameter, Octadecyl Prep LC packing, Bakerbond) instead of a non-polar organic solvent to separate hydrophobic colloids.

The method was applied to goethite particles treated with  $\text{NaH}_2\text{PO}_4$  and  $\text{Al}(\text{NO}_3)_3$  at different pH values (triplicate samples). The suspensions were filtered over a 15  $\mu\text{m}$  Nylon mesh (Nybolt) prior to turbidity measurements (T1). Thirty mg of C18 microparticles and 10 mL of suspension were mixed in a glass tube allowing for hydrophobic colloids to sorb onto their surface. The tubes were put on a horizontal shaker (KS501digital, IKA Labortechnik) at 100 rpm for 2 hours. At the end of the shaking period, C18 particles were separated using the 15  $\mu\text{m}$  Nylon mesh and the turbidity of the filtered suspensions was determined (T2). Hydrophobicity was calculated according to equation (2.1) in section 2.3.3.

### 2.3.3 Calculation of hydrophobicity

The calculation of hydrophobicity (H) is based on the distribution coefficient of colloids between a polar and an apolar phase as described by Guiné et al. (2003). The turbidity of the colloidal suspension is measured prior (T1) and after (T2) the extraction of hydrophobic colloids. Hydrophobicity is then calculated according to equation (2.1).

$$H = \frac{T1 - T2}{T1} \quad (2.1)$$

#### **2.3.4 Further optimization of the C18-method**

In order to determine the optimal quantity of C18 microparticles required for a certain turbidity of the suspension we conducted a capacity test. Microparticle aliquots from 10 to 120 mg were shaken with 10 mL of filtered (15  $\mu\text{m}$ ) suspension of P-treated goethite particles. The sorbed quantity of goethite particles was determined using turbidity measurements as described in section 2.3.2.2.

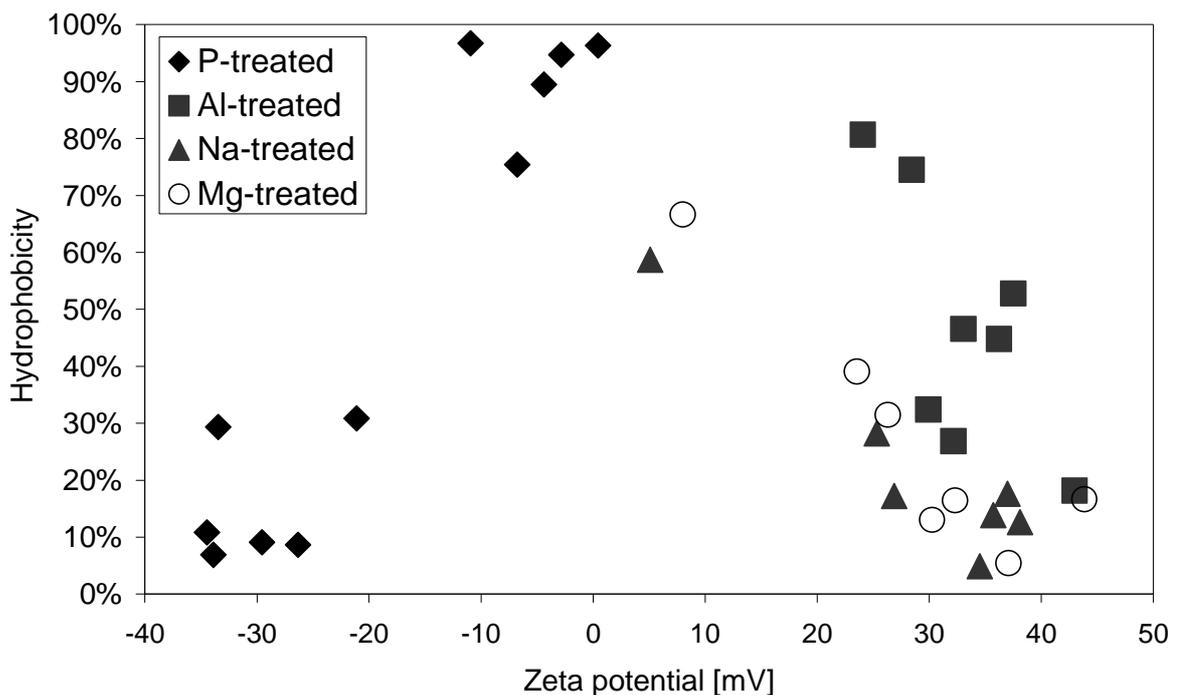
In order to determine the optimal shaking time we added 10 mL of goethite suspension (previously treated with  $\text{NaH}_2\text{PO}_4$ ) to 30 mg of C18 microparticles. The mixtures were put on a horizontal shaker (100 rpm) for 1, 2, 3, and 4 hours. Particle separation and turbidity measurements were conducted as described in section 2.3.2.2.

To test any competitive displacement between dissolved organic carbon (DOC) in soil solutions and hydrophobic colloids from the C18 microparticles we exposed the microparticles to a DOC solution. This solution was obtained from the aqueous extract of forest floor samples (100 g litter, 500 mL of deionised water), which was left to stand for 24 hours and subsequently filtered (prefiltered: folded filter (Sartorius, 132); 0.45  $\mu\text{m}$  cellulose-acetate (Sartorius, Type 11106 – 47 – N)). Dissolved organic C concentration of the extract was measured by a total organic carbon analyser (TOC – 5050 A, Shimadzu). Solutions of 20 and 100 mg DOC  $\text{L}^{-1}$  were chosen to represent average and high DOC concentration of aqueous soil extracts. They were prepared by appropriate dilution of the forest floor extract using deionised water. 10 mL of each solution were added to 30 mg C18 microparticles (triplicates) and equilibrated for 2 hours on a horizontal shaker at 100 rpm. The solution was filtered over a 15  $\mu\text{m}$  nylon mesh that had been previously rinsed with deionised water. The retained microparticles were then rinsed with deionised water and air-dried on the mesh. 10 mL of a suspension of P-treated goethite particles were added to 30 mg DOC-treated (DOC-20; DOC-100) as well as to untreated C18 microparticles. The suspensions were equilibrated, filtered and their turbidity determined as described in section 2.3.2.2.

## 2.4 Results and Discussion

### 2.4.1 Dichlormethane-Method

The results show a clear relation between the zeta potential and the hydrophobicity and are in line with our assumption (figure 2.1). The hydrophobicity determined by the two phase extractions of Al-treated goethite was higher than the Na- and Mg-treated versions at a similar absolute surface charge. These results may be explained by the interaction of Al with the organic solvent. Aluminium forms transition complexes with the chlorinated solvent as described in the Diels-Alder-Reaction (Fichte, 1986). Therefore, this method has some limitations and may only be applied to soils with little or no Al. The second, alternative method using C18-microparticles is supposed to overcome not only the problem of phase separation of the adapted method of Guiné et al. (2003) but also Al interactions (DCM-method).



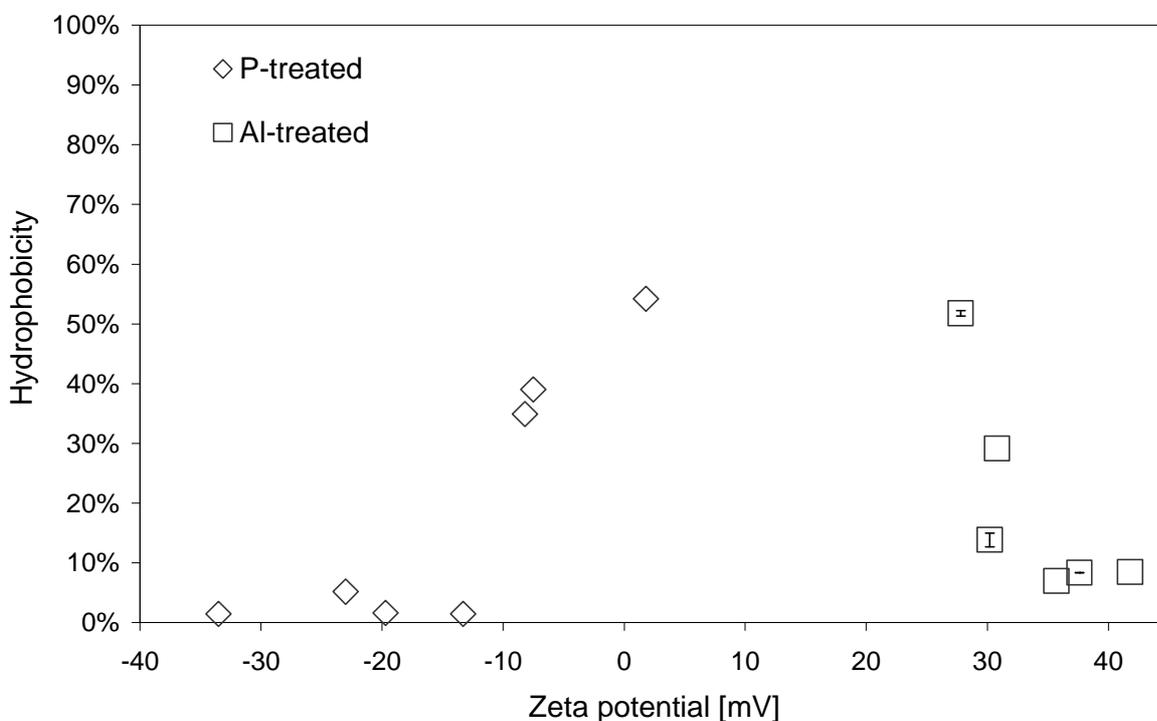
**Figure 2.1:** Hydrophobicity of differently treated goethite (as determined with dichlormethane) as a function of the zeta potential

### 2.4.2 C18-Method

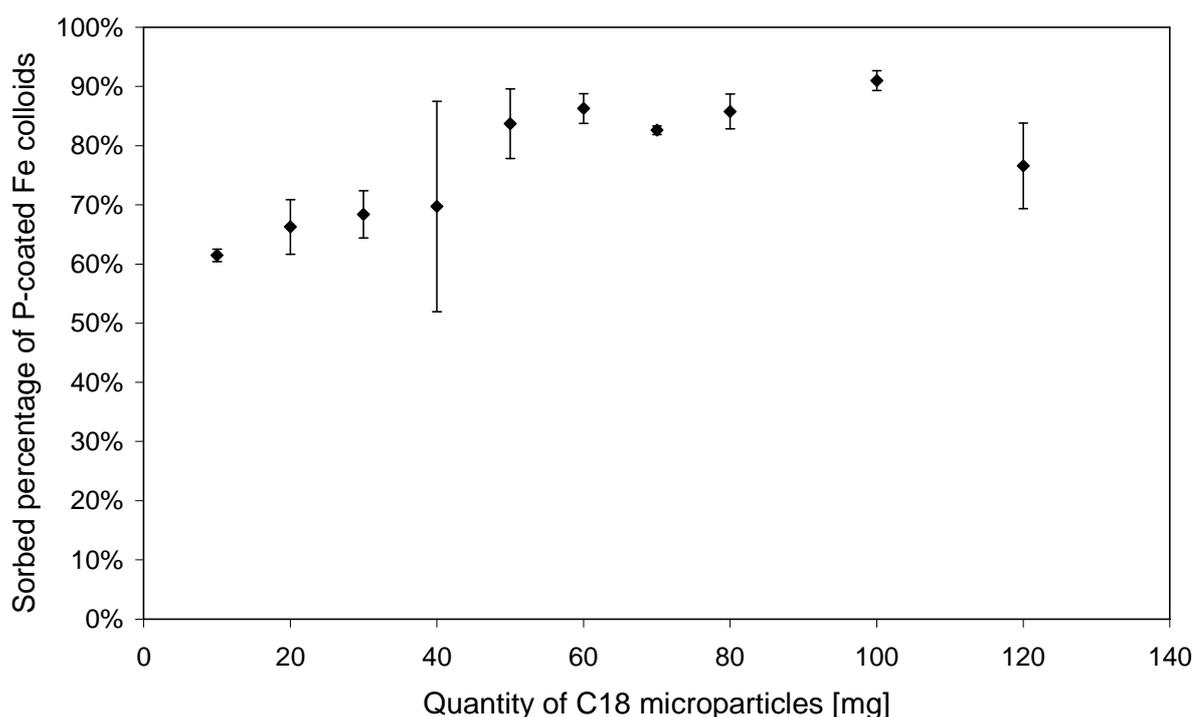
These results are similar to those found using the DCM-method, with a clear relationship between the zeta potential and the hydrophobicity (figure 2.2). The data

“gap” between the points at 1.8 mV (P-treatment) and 27.8 mV (Al-treatment) is explained by the high coarseness of the Al-coated goethite particles in that charge range, preventing them from being able to pass through the 15  $\mu\text{m}$  Nylon mesh. The relative maximum of H is a function of the particle surface characteristics and amounts to 54 % for the P- and Al-coated goethite particles.

The result of the capacity test is displayed in figure 2.3. This graph indicates that 60 mg microparticles per 12 FNUs is the optimal quantity (sorption maximum). However, if this amount was extrapolated to higher turbidity values (50 FNU), the C18 microparticles started to coagulate and resulted in lower uptake values than smaller quantities of microparticles. Therefore, we derived an optimal quantity of 30 mg, which may be used for suspensions of a turbidity up to 35 FNU (which is according to our experience a relatively high amount of dispersed colloids found in extracts of sandy soils, and much higher than the FNU of the soil solution). The different shaking times did not show any significant variation in the sorbed amounts of colloids (results not shown) and we chose to conduct the main experiment with a shaking time of 2 hours.



**Figure 2.2:** Hydrophobicity of Al- and P-treated goethite (as determined with C18 microparticles) as a function of the zeta potential



**Figure 2.3:** Capacity test of C18 microparticles (error bars depict one standard deviation)

The comparison of DOC-treated (DOC-20) with untreated C18 microparticles showed no significant difference in the quantity of the sorbed goethite particles (table 2.1). However, at very high DOC concentrations (DOC-100) a slight difference could be detected. This may be attributed to sorption of organic molecules to the C18-material. Therefore, we recommend the application of this method to soil solutions of no more than 20 mg DOC l<sup>-1</sup>.

**Table 2.1:** Result of the comparison between goethite particles sorbed on DOC-treated and untreated C18 microparticles (VC: variation coefficient)

	<b>DOC-100</b>	<b>DOC-20</b>	<b>Untreated</b>
<b>Average</b>	62.3 %	53.4 %	50.7 %
<b>VC</b>	5.2 %	8.8 %	5.2 %

## 2.5 Conclusion

The C18 method as described can be used for the determination of hydrophobic colloids in soil suspensions. The application of our method can help to better relate the properties of soil colloids to their function as carrier of pollutants in soils.



# 3 Hydrophobicity of Soil Colloids and Heavy Metal Mobilization – Effects of Drying

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## 3.1 Abstract

Drying of soil may increase the hydrophobicity of soil and affect the mobilization of colloids after re-wetting. Results of previous research suggest colloid hydrophobicity to be an important parameter in controlling the retention of colloids and colloid-associated substances in soils. We tested the hypothesis that air-drying of soil samples increases the hydrophobicity of water-dispersible colloids and whether air-drying affects the mobilization of colloid-associated heavy metals. We carried out batch experiments with field-moist and air-dried (25°C) soils from a former sewage farm (sandy loam), a municipal park (loamy sand), and a shooting range site (loamy sand with 25 % C<sub>org</sub>). The filtered suspensions (< 1.2 µm) were analyzed for concentrations of dissolved and colloidal organic C and heavy metals (Cu, Cd, Pb, Zn), average colloid size, zeta potential, and turbidity. The hydrophobicity of colloids was determined by their partitioning between a hydrophobic solid and a hydrophilic aqueous phase. Whilst drying increased hydrophobicity of the solid phase it did not affect the hydrophobicity of the dispersed colloids. Drying decreased the amount of mobilized mineral and (organo-)mineral colloids in the sewage farm soils, but increased the mobilization of organic colloids in the C-rich shooting range soil. Dried samples released less colloid-bound Cd and Zn than field-moist samples. Drying-induced mobilization of dissolved organic C caused a redistribution of Cu from the colloidal to the dissolved phase. We conclude that drying-induced colloid mobilization is not caused by a change in the physico-chemical properties of the colloids. Therefore, it is likely that the mobilization of colloids in the field is caused by increasing shear forces or the disintegration of aggregates.

### 3.2 Introduction

The influence of drying on the physico-chemical properties of the soil solution and the solid phase has been well researched. Dried soil samples showed a drastic increase in the concentration of dissolved organic matter (DOM) after rewetting (Bartlett and James, 1980; Baskaran et al., 1994; Courchesne et al., 1995; Münch et al., 2002; Kjærgaard et al., 2004b), leading to a decrease in the pH of the soil solution (Courchesne et al., 1995). The observed increase in DOC concentration may be attributed to the disruption of microbial biomass (Christ and David, 1996) and the breakdown of aggregate bonds (Raveh and Avnimelech, 1978). As DOC contributes to an enhanced mobilization of dissolved heavy metal species by forming soluble metal complexes (Brümmer et al., 1986) drying and rewetting may also be conducive to enhancing metal leaching. In addition, drying was also found to increase water repellency of the solid phase (Dekker et al., 2001), due to increasing hydrophobicity.

Numerous recent studies showed that colloid-bound heavy metal transport plays a crucial role in soils (Keller and Domergue, 1996; Jensen et al., 1999; Denaix et al., 2001) and is found to be of greater importance than transport as dissolved ions (Egli et al. 1999; Jensen et al., 1999). Several authors describe the influence of drying and rewetting as important factors controlling colloid release. El-Farhan et al. (2000) observed the highest peak of particle mass recovery after the infiltration on an initially dry field soil. Similarly, field studies of Jann et al. (2002) revealed increasing mobilization of colloids following dry periods. The authors attributed this phenomenon to micro-erosion and abrasion induced by shear forces. Likewise, Denaix et al. (2001) found markedly increased concentrations of mobilizable Pb-containing colloids in the soil water after dry periods. However, the drying-induced mobilization of colloids seems to be limited to the initial phase of re-wetting: In the frame of column studies using dried soil (soil-water potential: 15500 hPa) Kjærgaard et al. (2004b) observed an initial increase in colloid release followed by a constant decrease as the number of pore volume increases. This initial increase may be explained by slaking of aggregates due to the compression by trapped air during the wetting phase (Le Bissonnais, 1996). In the same study, Kjærgaard et al. (2004b) investigated the effect of initial soil matrix potential on water-dispersible colloids,

revealing that as a result of enhanced interparticle bonding or cementation of colloids drying leads to a decrease of dispersible colloids in the soil suspension.

As drying of soil may induce changes in the solid phase such as increasing hydrophobicity it is postulated that this may impact on colloid dispersibility. Few studies provide first hints on colloid hydrophobicity as an important parameter influencing colloid retention in soils. Wan and Wilson (1994a) demonstrated an increased retention of colloidal latex particles and bacteria with increasing particle hydrophobicity in an unsaturated sand column experiment. Similarly, under saturated conditions hydrophobic colloids showed a lower recovery than hydrophilic colloids. Thus, the authors concluded that hydrophilic colloids are more mobile than hydrophobic ones (Wan and Wilson, 1994a,b) since they sorb less strongly to the gas-water and solid-water interfaces. These findings, together with the observation that drying can increase the hydrophobicity of the bulk soil, are in conflict with the concept of colloid mobilization after soil drying. In addition to having an impact on colloid mobilization, colloid hydrophobicity also plays a key role in metal bioavailability. Carvalho et al. (1999) reported that the relative hydrophobicity of metal-colloid complexes may affect their bioavailability by enhancing their transport across membrane lipid bilayers.

In addition to directly affecting colloid properties, drying and rewetting of soils may affect the dispersibility of colloids by altering the physico-chemical properties of the soil solution, for example increasing DOC concentration of the soil solution is known to enhance colloid stability (Kretzschmar et. al., 1999).

Moreover, air-dried soils are commonly used for various soil analyses. Whereas it is well documented that heavy metal as well as organic C concentrations in the extracts of air-dried and moist soils differ from each other (Wang et al., 2002; Tom-Petersen et al., 2004), studies of the effect on the colloid-bound fractions are absent. Thus, the results of this study may provide important information for the design of analytical procedures.

As the effect of drying-induced hydrophobization on the amount and properties of dispersible colloids has not been investigated and the underlying mechanisms of colloid release after drying are unknown the aim of this paper was to investigate whether

- (a) drying of soil samples does not only increase the hydrophobicity of the solid phase but also the hydrophobicity of dispersible colloids.
- (b) drying of soil samples increases the colloid-bound as well as dissolved metal fractions.

### **3.3 Material and Methods**

#### **3.3.1 Soil Samples**

The experiments were conducted with soil samples taken from the A<sub>n</sub> horizons of the Berlin sewage farm (Buch soil) classified (according to World Reference Base for Soil Resources, 1998) as Regosol with sandy clay loam texture and the Berlin municipal park Tiergarten (TG) classified as Cambisol with sandy loam. They are both developed on quaternary fluvial sands, however, the sediment structure of the Tiergarten park has been changed at the beginning of the last century by adding building rubble and dredged lake sediment. Both sites were chosen since they were contaminated by heavy metals due to the impact of sewage water (Buch soil) and building rubble (TG soil). The experimental site on the sewage farm has been divided into 3 subplots of similar texture (hence the labeling B1, B2, B3). The entire site is characterized by a high small-scale heterogeneity. Additionally, we investigated the top soil (0 – 10 cm) of a former shooting range site near Gütersloh (GS), Lower Saxony, Germany, where oak trees have been growing for the past 30 years. The soil is a podzolic Cambisol with a texture of loamy sand. It developed on fluvial sandy stream deposits of the Pleistocene. This soil was included in the study due to its high contamination by Pb, which is known to have a high affinity to colloids (Egli et al., 1999; Jensen et al., 1999; Denaix et al., 2001) and because of its high

content of organic matter. We sampled the A<sub>eh</sub> horizon, which was interrupted by the forest floor O<sub>h</sub>-horizon. For the analyses we mixed both horizons.

The samples were homogenized and sieved (2 mm) after the removal of roots and stones. The soils did not contain any significant amounts of aggregates before homogenization and sieving. The field-moist soil samples were put in plastic bags and stored in a refrigerator. An aliquot of the samples was dried at 25 °C until constant weight and kept in air-tight plastic containers at room temperature until use.

To characterize the soil samples the pH was determined in de-ionised water and 0.01 M CaCl<sub>2</sub> solution, using 10 g of air-dried soil and 25 ml of the respective solution. The suspension was left to stand over night before the pH was measured using WTW inoLab pH-meter. Concentrations of organic C, N and S (C<sub>org</sub>, N<sub>org</sub>, S<sub>org</sub>) were measured by a C/N/S-analyzer (Elementar, vario EL III) with soil dried at 105°C. From these parameters, the C/N-ratio was derived. For the determination of the water content, field-moist samples were dried at 25 °C and 105 °C, until constant weight. Table 3.1 shows the analyzed properties of the sampled soil horizons. Total metal concentrations of the soil were determined by nitric acid-assisted digestion in closed vessels (180°C, 6 hours). After cooling, the digested samples were filtered (Schleicher & Schuell, Ø 150 mm, type 0790 ½, Ref. No. 10301645), transferred into 25 mL volumetric flasks, and subsequently filled to the mark with deionised water. The solutions were analyzed for Pb, Cu, Cd and Zn concentrations. For measurement details refer to section “analyses”.

The mobilization of colloidal and dissolved C, Cd, Cu, Pb and Zn was studied using triplicate field-moist and air-dried (25 °C) samples (< 2 mm).

**Table 3.1:** Properties of the soil samples used for the experiments (n. d.: not determined)

Soil parameter	B1	B2	B3	TG	GS
pH <sub>H2O</sub>	5.7	4.7	5.5	4.1	3.6
pH <sub>CaCl2</sub>	5.1	4.2	5.0	3.9	2.9
Conductivity [dS m <sup>-1</sup> ]	0.135	0.184	0.268	1.473	0.195
C <sub>org</sub> [g kg <sup>-1</sup> ]	50.0	29.0	22.0	56.0	245.0
N <sub>tot</sub> [g kg <sup>-1</sup> ]	5.0	3.0	2.0	4.0	9.0
S <sub>tot</sub> [g kg <sup>-1</sup> ]	1.6	0.8	0.5	3.1	n. d.
C/N ratio [-]	9.7	9.3	11.4	12.5	27.0
Pb [mg kg <sup>-1</sup> ]	132	86	248	141	11 000
Zn [mg kg <sup>-1</sup> ]	528	559	1218	37	n. d.
Cd [mg kg <sup>-1</sup> ]	9	12	38	1	n. d.
Cu [mg kg <sup>-1</sup> ]	72	55	265	67	n. d.
Water content (25 °C) [wt.%]	9.7	10.8	13.5	18.8	46.4
Water content (105 °C) [wt.%]	9.9	10.9	16.2	19.4	47.4

### 3.3.2 Experimental setup

Based on the procedure of Curtin et al. (1994), who used a soil to water ratio of 1:10 to determine clay dispersibility, we chose a soil to water ratio of 15 g field-moist soil to 150 ml total solution volume in combination with turbidity measurements (see below). The weight of the dried soil samples was corrected for the loss of water. Samples were shaken for 16 hours, using an end-over-end-shaker (18 rpm; GFL 3040).

At the end of the experiment pH and conductivity were measured in the suspensions prior to filtration (1.2  $\mu\text{m}$  cellulose-nitrate filter, Sartorius, Type 11303 – 047N). We determined total organic carbon concentrations (denoted as TOC in the following) as well as total concentrations of Cd, Cu, Pb, and Zn, turbidity, hydrophobicity, particle size, and zeta potential of the filtrate. An aliquot of the suspension was ultracentrifuged at 300 000  $g$  for 1 h at 10  $^{\circ}\text{C}$  (Beckman Optima TL) in order to separate colloids larger than 14 nm and a density  $> 1.2 \text{ g cm}^3$  (based on Stoke's law) from the solution. The supernatant was transferred into plastic vessels, acidified with nitric acid and analyzed for Cd, Cu, Pb, Zn and organic C (DOC) concentrations (considered as truly dissolved). The difference between concentrations in ultracentrifuged and not ultracentrifuged samples accounts for colloidal fractions (operationally defined) of the above mentioned elements.

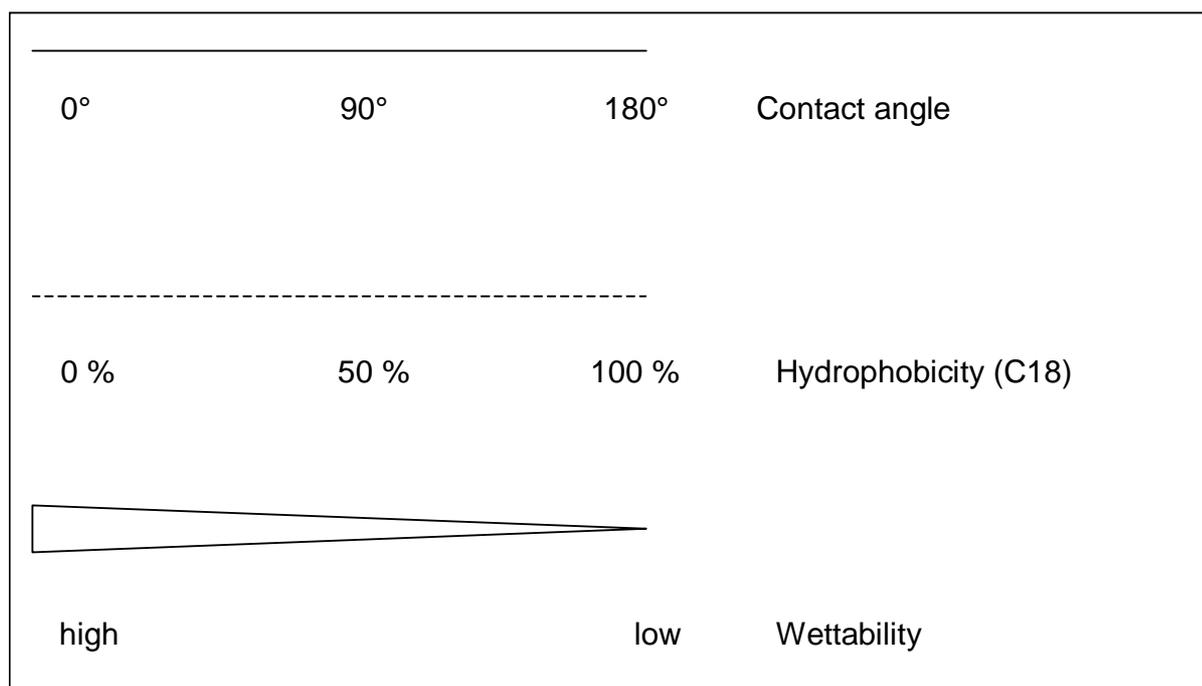
### **3.3.3 Analyses**

Cadmium, Cu, Pb and Zn concentrations of the colloidal suspensions were determined after microwave-assisted nitric acid digestion (CEM, MARS Xpress) according to the procedure described in EPA method 3015 (EPA 1994). The Zn measurement was carried out using a flame atomic absorption spectrophotometer (Perkin Elmer 1100 B) at a wavelength of 213.7 nm. Copper, Pb and Cd analyses were determined using a graphite furnace atomic absorption spectrophotometer (Varian, Spectra AA 880Z; wavelength: 327.4 nm, 283.3 nm and 228.8 nm, respectively). The organic C concentration of the suspensions and solutions was measured by a total organic carbon analyser (TOC – 5050 A, Shimadzu). The turbidity was determined by a turbidimeter (Hach 2100P ISO). Hydrophobicity of the colloids was measured as a partitioning coefficient between the aqueous suspension and a solid hydrophobic phase ( $\text{C}_{18}$  Prep LC Packing, diameter: 40  $\mu\text{m}$ , Bakerbond, Type 7025 – 00). Ten mL of filtered suspension were added to 30 mg  $\text{C}_{18}$  spheres and shaken for 2 hours at 100 rpm (IKA Labortechnik, KS501 digital) in order to allow for hydrophobic colloids to sorb onto the solids. Afterwards, the suspensions were filtered over a 15  $\mu\text{m}$  Nylon gauze to remove the  $\text{C}_{18}$  spheres. The turbidity (T2) of the filtrate obtained was re-measured. Hydrophobicity (H) was calculated according to the following formula (equation 2.1):

$$H = \frac{T1 - T2}{T1} \quad (2.1)$$

with T1 being the turbidity of the suspension prior to C<sub>18</sub> treatment. Further details about the method are described in Klitzke and Lang (2007).

The contact angle of the bulk soil samples as a measure for hydrophobicity of the solid phase was determined by indirect measurements. The field-moist samples were measured by the capillary rise method as described by Adamson (1990) and air-dried samples by the Wilhelmy plate method (Bachmann et al., 2003). The use of two methods was considered essential due to the different wettabilities of the samples caused by the drying process. Figure 3.1 depicts the relation of the 3 parameters contact angle, hydrophobicity as determined by C<sub>18</sub> spheres and wettability.



**Figure 3.1:** Relation between contact angle, hydrophobicity and wettability

The size distribution of the colloids was analysed by dynamic light scattering (HPSS – High Performance Particle Size, Malvern Instruments) and from the calculated particle size distribution curve (based on the volume) an average diameter was read

off. The Zeta potential was determined by a Zetasizer 2000 photon correlation spectrometer (Malvern Instruments) on the basis of electrophoretic mobility measurement of the colloids.

For each parameter of the complete sample set a paired t-test was conducted to determine significant differences between results from field-moist and air-dried samples. Since the properties of the Gütersloh soil differ greatly from the other soils included in the study, a second t-test was carried out based on the Buch and Tiergarten soils only. In addition, statistically significant differences between the triplicates of field-moist and air-dried samples of individual soils were determined by an unpaired t-test. We used a level of significance of 95 % ( $P < 0.05$ ) for both tests.

### 3.4 Results and Discussion

Statistically significant differences for each parameter of the complete sample set between field-moist and air-dried samples are displayed in table 3.2. In that context it has to be mentioned that the results of the t-test are only a helpful tool if there are no inverse effects, i. e. if all soils show the same tendency (either increasing or decreasing concentrations of a parameter following drying). If this condition is not met, opposing effects cancel each other out and the result of the t-test is distorted. It has to be mentioned that the significance of effects for individual soils can be indirectly determined by the error bars displayed in the graphs, representing twice the standard deviation at a confidence level of 95 %.

**Table 3.2:** Significance of the effects of soil drying on the given soil characteristics, (+) indicates statistically significant differences between field-moist and air-dried samples ( $P < 0.05$ ). They relate to assessed parameters across all examined soils.

Pb <sub>diss</sub>	-	Cu <sub>diss</sub>	-	Cd <sub>diss</sub>	-	Zn <sub>diss</sub>	-	DOC	+
Pb <sub>coll</sub>	-	Cu <sub>coll</sub>	-	Cd <sub>coll</sub>	+	Zn <sub>coll</sub>	+	COC	-
Contact angle	+	Turbidity	-	Hydrophobicity	-	Zeta potential	-	pH conductivity	-

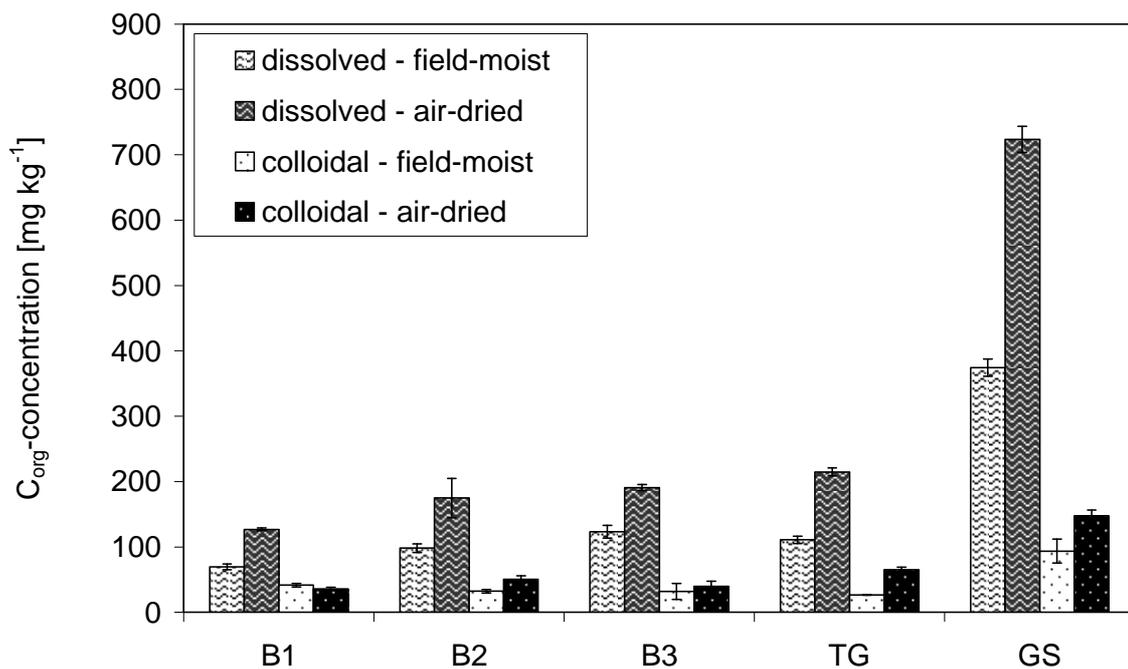
**3.4.1. Influence of drying on the composition of the dissolved phase**

For most of the soil samples drying did not lead to a major, significant change in pH and conductivity (table 3.2 and 3.3). In the case of the Gütersloh soil the observed increase in conductivity following drying may be attributed to the drastic increase in TOC of the suspensions.

**Table 3.3:** pH and electrical conductivity in suspensions (s:w ratio: 1:10) of field-moist and air-dried soil samples ( $\pm 1$  standard deviation)

Parameter	B1	B2	B3	TG	GS
pH suspension field-moist samples	5.6 $\pm$ 0.0	4.6 $\pm$ 0.0	5.5 $\pm$ 0.1	4.1 $\pm$ 0.0	3.7 $\pm$ 0.0
pH suspension air-dried samples	6.0 $\pm$ 0.1	5.0 $\pm$ 0.1	5.7 $\pm$ 0.3	4.2 $\pm$ 0.1	3.6 $\pm$ 0.1
Conductivity [dS m <sup>-1</sup> ] Suspension of field-moist samples	0.051 $\pm$ 0.001	0.086 $\pm$ 0.002	0.096 $\pm$ 0.003	0.760 $\pm$ 0.008	0.155 $\pm$ 0.003
Conductivity [dS m <sup>-1</sup> ] Suspension of air-dried samples	0.056 $\pm$ 0.001	0.086 $\pm$ 0.002	0.094 $\pm$ 0.003	0.738 $\pm$ 0.031	0.177 $\pm$ 0.002

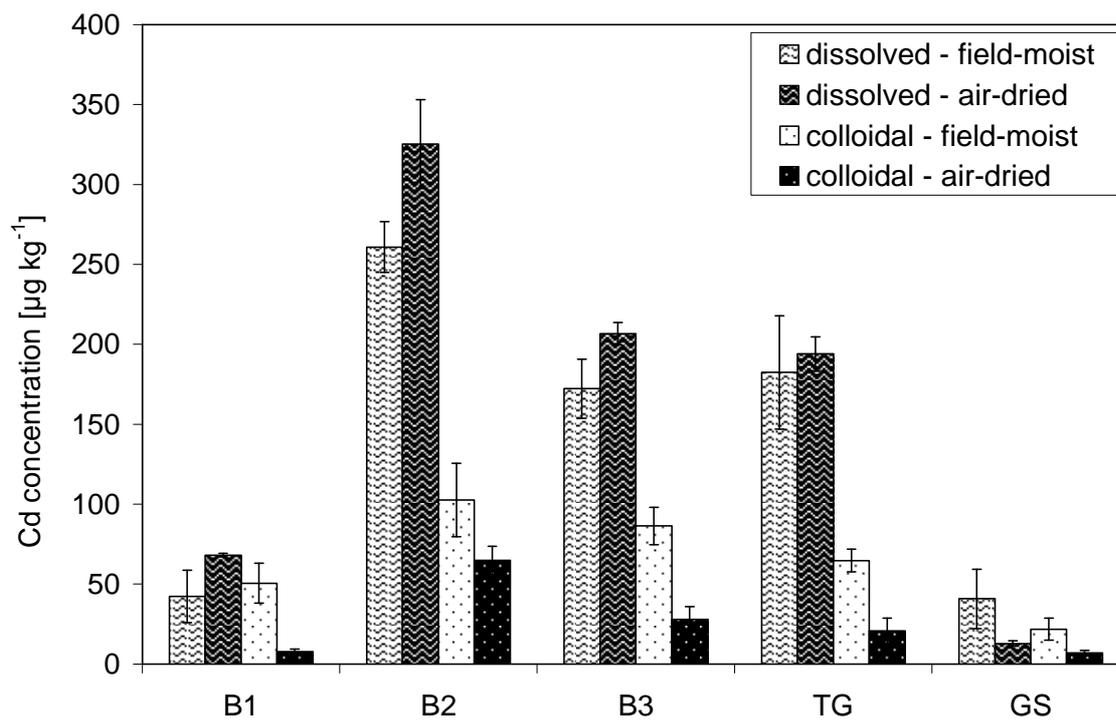
The DOC concentrations in the air-dried samples were significantly higher than concentrations in the field-moist samples (table 3.2), the change being especially pronounced for the Gütersloh soil (figure 3.2). These findings are in accordance with observations reported by Baskaran et al. (1994), Courchesne et al. (1995), and Kaiser et al. (2001).



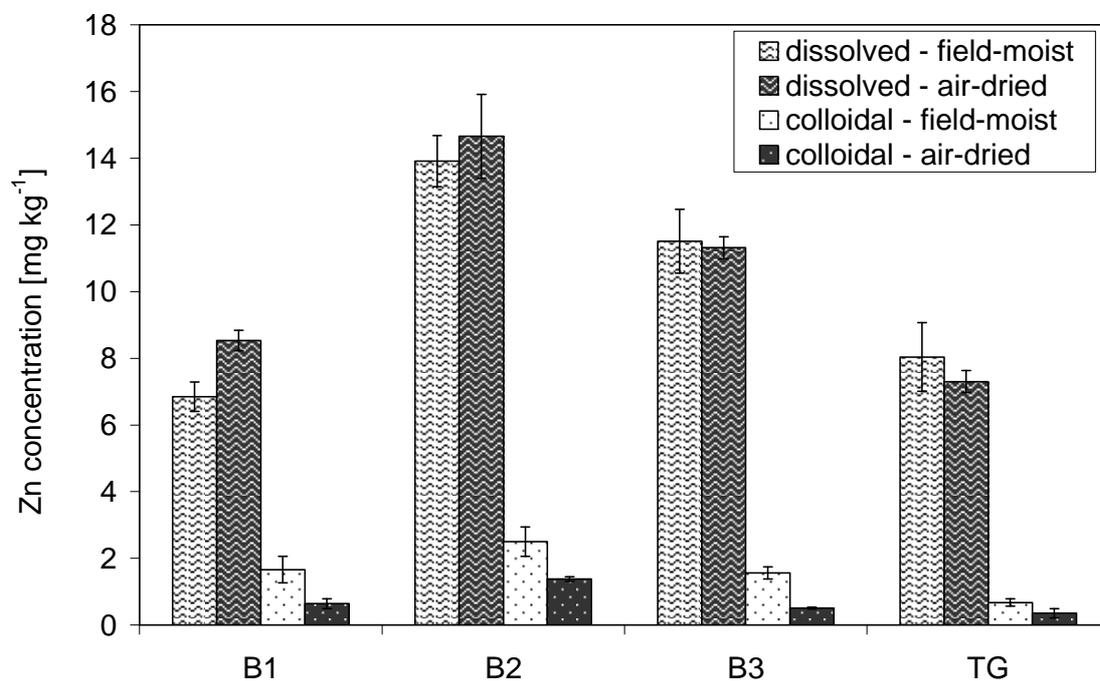
**Figure 3.2:** Dissolved and colloidal  $C_{org}$  concentrations in suspensions of field-moist and air-dried samples (error bars depict one standard deviation)

In most samples, drying did not lead to a significant increase in dissolved concentrations of Cd and Zn (figure 3.3a and 3.3b). As both metals have a very low affinity to organic C (McBride, 1994) their mobilization is not controlled by the increasing concentration of DOC.

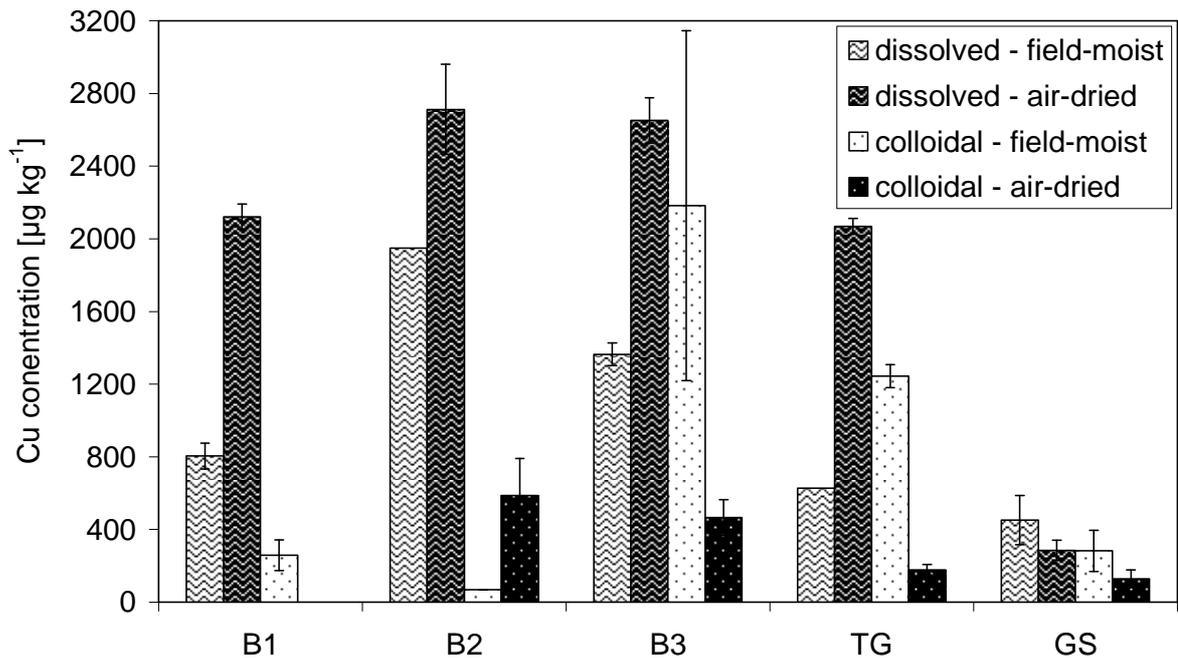
Dissolved Cu concentrations increased drastically following drying (fig 3.3c) and are statistically significant for all soils except for the Gütersloh soil. These findings are consistent with results reported by Tom-Petersen et al. (2004). The authors attribute this phenomenon to increased concentrations of dissolved organic C which leads to the formation of dissolved organic Cu complexes. The exception of the Gütersloh soil may be explained by the extremely high Pb concentrations, exceeding dissolved Cu concentrations by more than two orders of magnitude and therefore displace Cu from being complexed by DOC.



**Figure 3.3a:** Dissolved and colloidal Cd concentrations in suspensions of field-moist and air-dried samples (error bars depict one standard deviation)

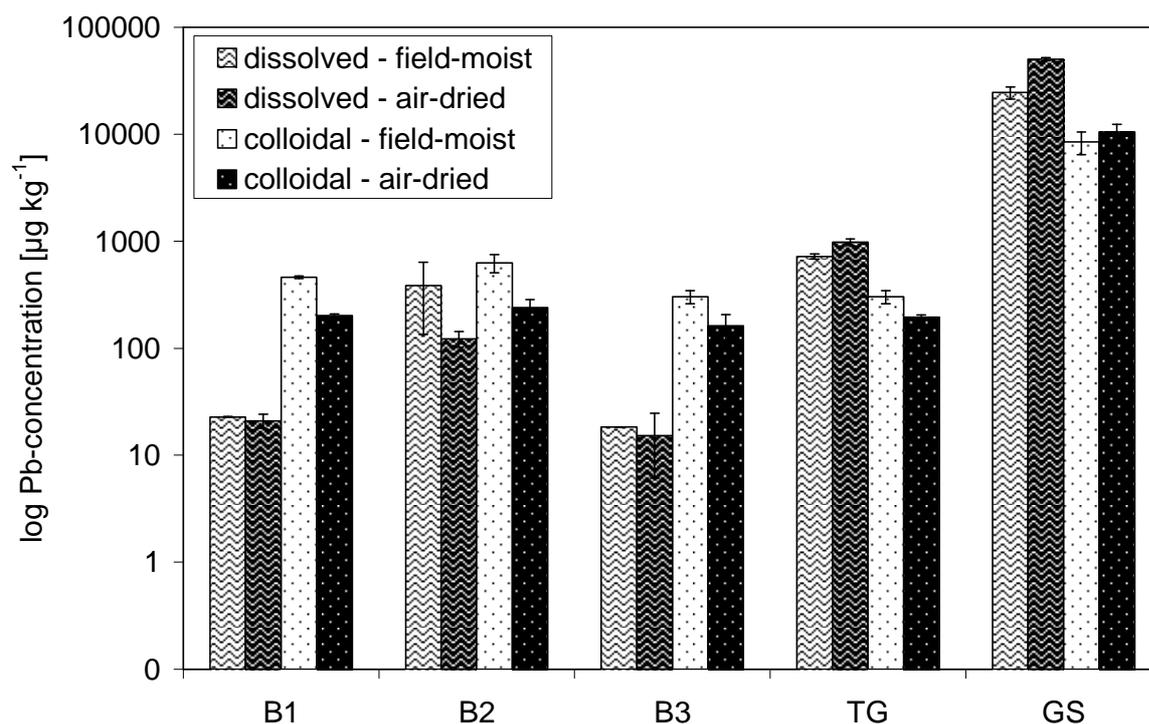


**Figure 3.3b:** Dissolved and colloidal Zn concentrations in suspensions of field-moist and air-dried samples (values of Gütersloh soil are below quantification limit; error bars depict one standard deviation)



**Figure 3.3c:** Dissolved and colloidal Cu concentrations in suspensions of field-moist and air-dried samples (error bars depict one standard deviation; air-dried colloidal concentrations of the B1 sample not determined)

In contrast to Cu, the effect of drying on the mobilization of dissolved Pb varied for the different samples. The Buch samples showed constant, the Tiergarten and the Gütersloh soils (according to the t-test) significantly increasing dissolved Pb concentrations after drying (figure 3.3d). In the Gütersloh soil the increase can be ascribed to the extremely high concentration of DOC, leading to the mobilization of dissolved organic Pb complexes (McBride, 1994). In the Buch soils we did not observe any increase in dissolved Pb concentrations despite increasing DOC concentrations. The higher affinity of Cu to soil organic matter (McBride, 1994) and the higher stability constants of Cu for humic acids (Lubal et al., 1998) and Cu-EDTA complexes (Lindsay, 1979) could explain why the drying-induced release of organic C does not lead to a mobilization of Pb in the Buch soils but to a preferred complexation of Cu. In the Gütersloh soil, however, the extremely high Pb concentrations exceed the Cu concentrations, therefore, despite the higher affinity of Cu for organic matter it is displaced by Pb from the organic complex.



**Figure 3.3d:** Dissolved and colloidal Pb concentrations in suspensions of field-moist and air-dried samples (error bars depict one standard deviation)

### 3.4.2. Influence of drying on the composition and properties of dispersible colloids

All analyzed soils had substantial amounts of colloids in the suspension except for the Tiergarten soil, which hardly releases any colloids at all.

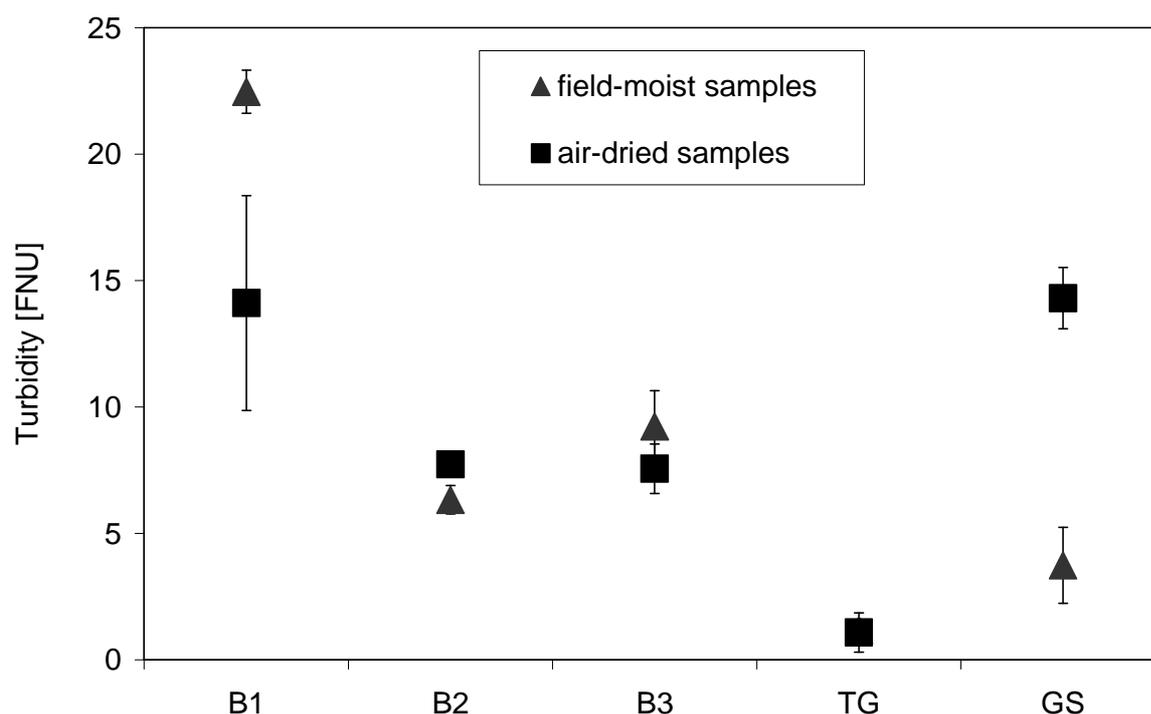
Based on turbidity measurements, the statistical analysis of all samples does not show any significant effect of drying on the mobilization of colloids (table 3.2). This is because drying shows inverse effects for different soil samples: The Gütersloh soil shows increasing colloid mobilization after drying, while the Buch soils show a decreasing and the Tiergarten soil constant number of mobilized colloids following drying. Therefore, in the statistical analysis, two opposing effects “cancel” each other out. The decrease and constancy in colloid mobilization are in contrast to results obtained from field studies reported by Denaix et al. (2001) who conducted their study on soil of similar texture and pH and Jann et al. (2002; calcareous gravel), indicating colloid mobilization after re-wetting of dry soil. However, decreasing colloid

concentrations are supportive of findings in sandy soils of different clay content as reported by Kjærsgaard et al. (2004a,b).

The decreasing amount of mobilized colloids may be explained by three processes:

- (I) Enhanced aggregation during the drying process as described by Thill and Spalla (2003).
- (II) Drying-induced disintegration of organomineral complexes as suggested by Peltovuori and Soinne (2005). The break up of weak bonds between organic matter and hydroxides (Haynes and Swift, 1989) may reduce the stability of mineral colloids resulting in a decrease in colloid mobilization.
- (III) Hydrophobization of colloids as will be explained in the following paragraph.

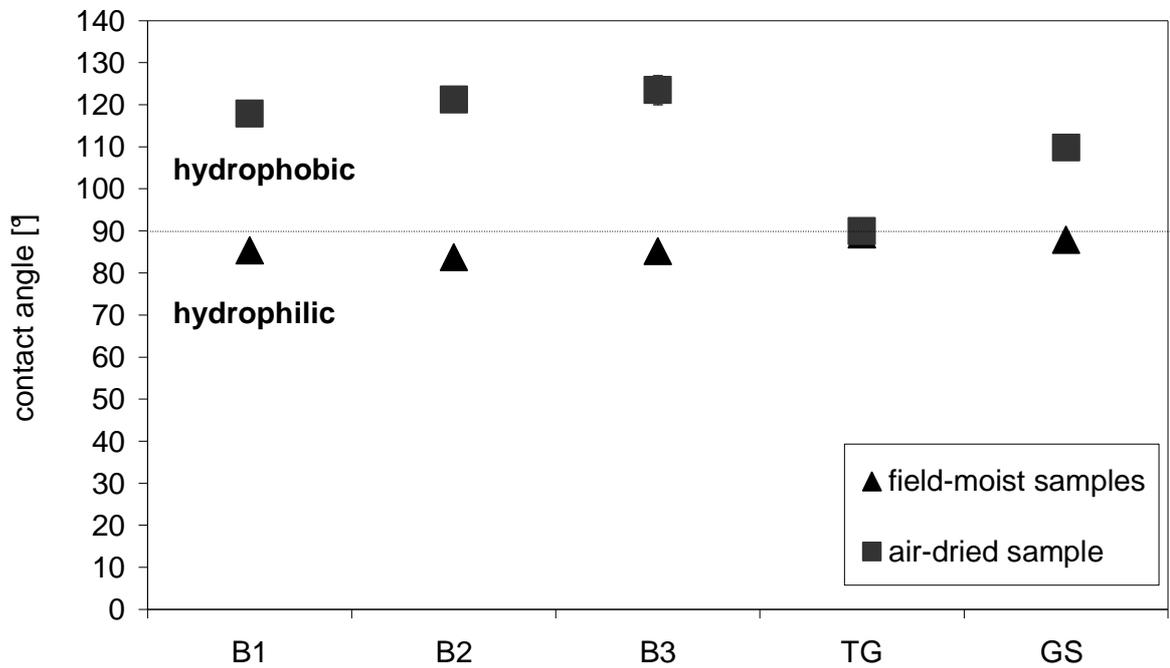
The difference in changes of turbidity was most pronounced for the samples B1 and Gütersloh. Whereas soil B1 demonstrated a decrease in turbidity following drying, the Gütersloh soil showed the opposite (figure 3.4). The high content of organic matter of the latter creates the potential for a 3-dimensional network forming under field-moist conditions (Schaumann et al., 2000). Such a cross-linked gel structure of organic material could possibly impede the release of colloids into the solution. In previously dried soil, however, any such restrictive network that existed would have likely been destroyed and would take time to re-develop. Thus, upon rewetting, colloids would initially be able to move freely into solution, resulting in an enhanced release of colloids. An additional factor that may have contributed to the increased release of colloids from the organic-rich Gütersloh soil is thought to be the disruption of biomass (Christ and David, 1996) and possible release of organic matter associated with microbial death and cell lysing upon drying. The higher initial water content of the Gütersloh soil may also have been a factor.



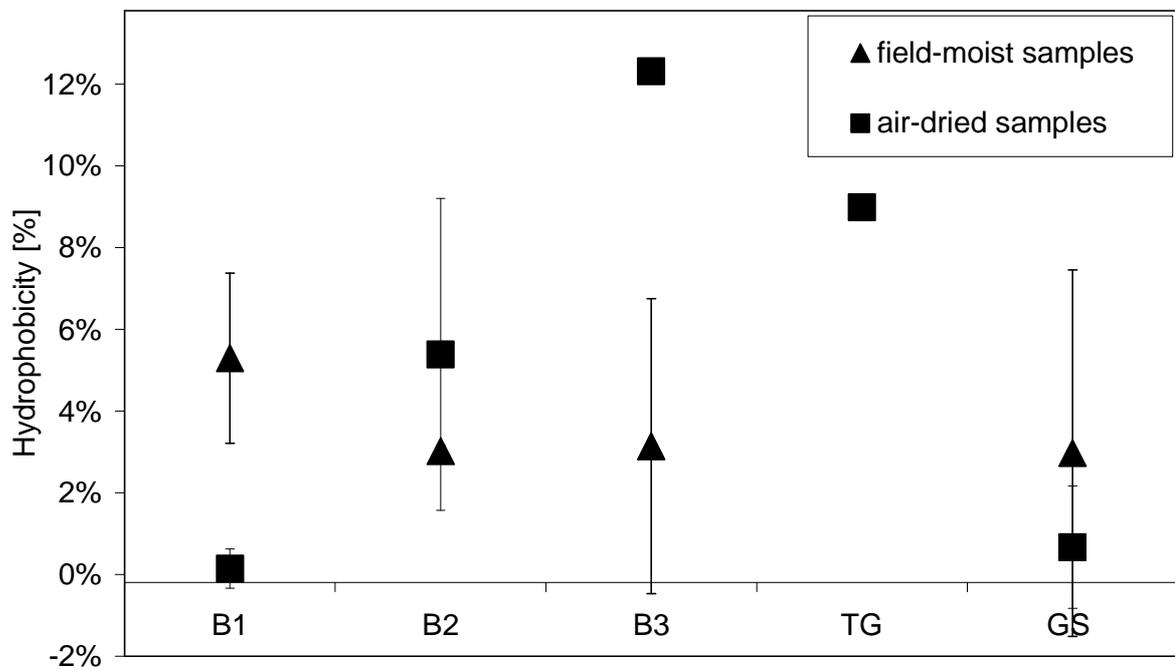
**Figure 3.4:** Turbidity in the soil suspensions of field-moist and air-dried samples (error bars depict one standard deviation)

With the exception of the Tiergarten samples our results demonstrate a significantly increasing contact angle of the solid phase following drying (figure 3.5, table 3.3), which is consistent with an increasing water repellency (Goebel et al., 2004). This result implies that drying increases hydrophobicity and agrees with observations reported by Dekker et al. (2001) and Hurraß and Schaumann (2006). Surprisingly, the change in hydrophobicity of the dispersible colloids does not follow the change in hydrophobicity of the solid sample. We observed smaller changes in the hydrophobicity of the colloids, but in general they remained hydrophilic (figure 3.6). We postulate drying renders the colloids of the solid phase hydrophobic but these hydrophobic colloids are no longer suspended after drying. This assertion is supported by the work of Wan and Wilson (1994 a,b) who observed that hydrophobic colloids are less mobile. As a result only colloids which are not affected by the hydrophobization process, i. e. hydrophilic ones, are found in the analyzed suspensions. Another possible explanation for the occurrence of hydrophilic colloids is the presence of amphiphilic organic molecules as they were found to be an important factor controlling wettability (Hurraß and Schaumann, 2006). Their non-polar groups are thought to sorb onto the hydrophobic surface whilst the polar

groups would point towards the aqueous phase rendering the surface hydrophilic and thus allowing better mobilization of colloids of hydrophobic samples.



**Figure 3.5:** Contact angle of field-moist and air-dried samples (error bars depict one standard deviation)



**Figure 3.6:** Hydrophobicity of colloidal suspensions of field-moist and air-dried soil samples (error bars depict one standard deviation)

Our findings indicate that drying of the soil does not lead to a major change in the physico-chemical properties of the suspensions: The Zeta potential as well as the particle size of the suspended colloids remained constant (data not shown). The extremely high conductivity values of the Tiergarten soil (table 3.2) account for a high ionic strength of the soil solution and explain the lack of colloids in the suspension.

Concentrations of colloidal organic C remained constant or showed an increase (figure 3.2) for most soils with the differences being most pronounced and statistically significant (t-test) for the Tiergarten and Gütersloh soils. Our results support the findings of Kjærgaard et al. (2004a,b) who observed an increase in colloidal organic C following drying. We explain this phenomenon by the disintegration of organomineral complexes (Peltovuori and Soinne, 2005) and the disruption of microbial biomass (Christ and David, 1996) in the C-rich Gütersloh soil.

Our results reveal no increase in the colloid-bound metal fraction (data not shown) as would be expected from suggestions in the literature (Denaix et al., 2001). We observed a clear decline in both concentrations and fractions of colloid-bound Cd and Zn (table 3.3). Our data suggests a preferential cementation of inorganic particles of the soil matrix induced by the drying process leading to a lower degree of colloid dispersibility after rewetting.

Colloid-bound Cu concentrations decreased in two soils following drying despite increasing colloidal organic C concentrations. This implies that there is no correlation between these two parameters although Cu has a high affinity to organic matter (McBride, 1994). These findings suggest: (I) Colloidal Cu in these soil suspensions may be mainly bound to inorganic particles, which may possibly have an organic surface coating. (II) Since the suspensions of air-dried samples showed elevated concentrations of DOC one might also hypothesize an equilibrium between colloidal Cu and dissolved organically complexed Cu, i. e. high DOC concentrations could lead to a desorption of Cu from the colloids. This assumption would be in line with increasing concentrations of dissolved Cu in the suspensions of the air-dried samples.

Whereas the drying process leads to a significant decrease in colloidal Pb concentrations for the Buch and the Tiergarten soils, concentrations remain constant in the Gütersloh sample. If the Gütersloh soil is left out in the t-test (table 3.3), changes for the Buch and Tiergarten soils are significant. This difference could be ascribed to the lower  $pH_{H_2O}$  and the high organic C content of the Gütersloh soil allowing for the formation of Pb-organic precipitates (Lang et al., 2005). However, the fractions of colloidal Pb for all soils (data not shown) remain unchanged by the drying process. For the Buch soils, colloidal Pb accounts for between 70 and 96 % of total Pb in suspension, whereas in the Gütersloh soil dissolved Pb is dominating. Similarly to Cu, the data set does not reveal any correlation between colloidal organic C and colloidal Pb. These findings lead to the conclusion that colloidal Pb in the Buch soils is predominantly bound to inorganic colloids.

### **3.5 Conclusion**

Our batch experiments showed that drying of the studied soils does not lead to a uniform increase in the concentration of water-dispersible colloids. We conclude that the influence of drying on the dispersibility of pedogenic colloids is likely to depend on their composition. In a C-rich matrix mainly organic colloids are mobilized by soil drying, whereas in a more mineral matrix (organo)-mineral colloids are immobilized, possibly due to enhanced cementation during the drying process. Drying-induced (im)mobilization of colloids does not always go along with the change in concentration of colloid-associated heavy metals. This indicates that drying does not only affect the mobilization of colloids but also the equilibrium between colloidal and dissolved species. Absolute concentrations of the investigated colloid-bound heavy metals were found to decrease in almost all soil samples for Cd and Zn, and in some soils, for Cu and Pb also. This decrease may either be attributed to the immobilization of colloids (as observed for Zn, Cd and in some samples also for Pb) or to the mobilization of heavy-metal sorbing DOM leading to a redistribution of the metal between colloidal and dissolved phase (as observed for Cu). Since drying did not influence the physico-chemical properties of the colloids our results suggest that drying-induced colloid mobilization in the field is most likely due to shear forces (as already explained by Jann et al., 2002) or the dispersion of macroaggregates

(Kjærgaard et al., 2004a) rather than by a major change in physico-chemical properties of the colloids. Future studies should assess whether the presented results are also applicable to intact cores.

## 4 Increasing pH releases colloidal Lead in a highly contaminated Forest Soil

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### 4.1 Abstract

Colloids can play an important role in the leaching of lead (Pb) in soils, and liming to increase pH may produce conditions conducive to colloid release. We studied the effect of pH and the role of counterion valency on the mobilization of Pb in two topsoil horizons of a former shooting range. In batch experiments, the release of both dissolved and colloidal Pb was studied at a pH range between 3 and 7. The pH was adjusted with solutions of nitric acid (pH 3) and KOH and  $\text{Ca}(\text{OH})_2$  (pH 4 to 7) and the chemical composition, size and charge of the mobilized colloids were determined. In the presence of the monovalent  $\text{K}^+$ -ion concentrations of colloidal and dissolved Pb increased markedly with increasing pH. Colloids were stabilized not only by electrostatic but also by steric repulsion. Organic colloids seem to dominate at low pH of the KOH-treatment, at  $\text{pH} > 4$  mineral particles were also dispersed. Even though the presence of the  $\text{Ca}^{2+}$ -ion reduced the concentrations of colloidal Pb more than did the  $\text{K}^+$ -ion, our results of the  $\text{Ca}(\text{OH})_2$  treatment show that the relevance of both colloidal and dissolved Pb increases at a pH of about 5.8. Risk assessment on limed sites should therefore take into account both dissolved, and colloidal Pb in judging the likelihood of Pb leaching.

## 4.2 Introduction

The risk of ground water pollution by lead (Pb) is of particular interest at highly contaminated sites such as rifle ranges, where the soil can contain as much as 80.9 g Pb kg<sup>-1</sup> (Knechtenhofer et al., 2003). These sites are often in forests on acid soils. Liming the soil has frequently been proposed as a means to reduce the risk of Pb leaching from such sites (Illera et al., 2004; Grønflaten et al., 2005). Several investigations have analysed the effect of pH on the mobility of Pb in soils. They assessed the success of Pb immobilization by liming (Grønflaten et al., 2005) or the risk of Pb mobility by acidification (Illera et al., 2004). Generally, the solubility of Pb decreases with increasing pH up to its solubility minimum at pH 6 (Herms and Brümmer, 1984). At pH > 6, an enhanced release of soil organic matter promotes the formation of soluble organo-Pb complexes (Sauvé et al., 1998).

Recent studies have emphasized the significance of colloids for the translocation of strongly sorbing pollutants in soils. They have shown that colloids are transported much faster than conservative tracers (substances which show no interaction with the soil matrix and therefore percolate at the same speed as soil water), due to size exclusion and electrostatic repulsion from the soil matrix (McKay et al., 1993). Transport facilitated by colloids has also been suggested as a major pathway for Pb leaching from soils (Egli et al., 1999; Denaix et al., 2001). Colloids might explain the apparent contradiction between Pb leaching measured in soil and the strong affinity of Pb to the soil solid phase. However, in the context of environmental risk assessment of sites contaminated by Pb and soil remediation, attention is usually paid to only the mobilization of truly dissolved species (see, for instance, Tack et al., 1999). So far there have been only few studies on the role played by colloids in forest topsoil, which contain large concentrations of organic matter. Wang and Benoit (1996) suggested that colloid-bound Pb species might be of high relevance at the boundary between the forest floor and Ah horizon.

Increasing soil pH causes significant mobilization of colloids (Kaplan et al., 1996). This can be explained by the increasing negative surface charge of particles with increasing pH (Kretzschmar et al., 1993; McBride, 1994). This causes both stronger repulsion by the negatively charged soil matrix (Kretzschmar et al., 1993) and

decrease of interparticle attraction (Kaplan et al., 1997). As the surface charge increases, larger electrolyte concentrations are needed to collapse the electric double layer (Kaplan et al., 1996). Consequently, with increasing pH, colloidal suspensions remain stable even at large concentrations of background ions.

The valency of the dominating counterion in suspensions plays a key role in colloid stability: Whereas a monovalent cation tends to disperse colloids, multivalent cations tend to suppress dispersion. The bivalence of the  $\text{Ca}^{2+}$ -ion leads to a compression or even collapse of the diffuse double layer, facilitating particle aggregation. Besides, Kretzschmar and Sticher (1997) noticed that the stabilizing effect of organic matter is reduced by increasing concentrations of  $\text{Ca}^{2+}$ , which they thought might be due to a bridging effect of the divalent  $\text{Ca}^{2+}$ . Therefore, the addition of the divalent  $\text{Ca}^{2+}$  to the soil by application of lime is likely to destabilize the colloids. The resulting net effect of the stabilizing pH-effect and the destabilizing Ca-effect, however, is unknown. Furthermore, 'bridging' reactions between  $\text{Ca}^{2+}$  and dissolved organic matter as reported by Dahlgren and Marrett (1991) might generate new colloidal particles.

In summary, the literature suggests that there is little colloid-facilitated Pb transport in acid conditions, but with increasing pH the mobilization of colloidal Pb from soils must be expected in addition to the mobilization of organically complexed Pb. Even though the stability of colloids at high pH is well documented, we know of no studies on the detachment of colloids from soil with increasing pH. We suggest that those factors that increase colloidal stability should also mobilize the colloids in soil, an idea that has yet to be proved experimentally. Besides, as far as we know, no one has directly investigated the effect of increasing pH on the amount and type of Pb-containing colloids that can be mobilized. Furthermore, there are no estimates of colloidal Pb relative to dissolved species over a range of pH. Thus, our objectives were

- (1) to investigate the effect of pH on the mobilization of dissolved and colloidal Pb from a heavily contaminated soil,
- (2) to elucidate the mechanisms of colloid mobilization by determining particle size, zeta potential and chemical composition of colloids dispersed at various pHs, and

- (3) to investigate the role of the divalent  $\text{Ca}^{2+}$ -ion as opposed to the monovalent  $\text{K}^+$ -ion in the process of pH-induced colloid mobilization.

### 4.3 Materials and Methods

#### 4.3.1 Soil sampling and soil characterization

Samples were taken from a former shooting range in North Rhine-Westphalia, Germany, which was wooded with 30-year-old oak trees. The soil's parent material is a fluvial, sandy stream deposit of the Pleistocene. The soil itself is a Podzolic Cambisol on top of which is an Oh horizon of the forest floor. For one set of experiments we mixed Ah and Oh material (0 – 10 cm; to give soil 1) taken from two soil profiles, which we dug behind the former target. For the comparison of a pH increase in the presence of a divalent ( $\text{Ca}^{2+}$ ) cation we used soil samples of the same topsoil but not exactly at the same position (soil 2). Table 1 shows some basic properties of the soil horizons.

**Table 4.1:** Some properties of the analysed soils

	pH ( $\text{CaCl}_2$ )	pH ( $\text{H}_2\text{O}$ )	$\text{C}_{\text{org}}$ [ $\text{g kg}^{-1}$ ]	C/N	$\text{Pb}_{\text{tot}}$ [ $\text{g kg}^{-1}$ ]	$\text{Fe}_{\text{tot}}$ [ $\text{g kg}^{-1}$ ]
Soil 1	2.9	3.6	245	27	11.0	4.4
Soil 2	2.8	3.3	209	27	13.0	3.1

We determined the pH in deionized water and 0.01 M  $\text{CaCl}_2$  solution, using 10 g field-moist soil and 25 ml of the solution (pH Meter 761 Calimatic, Knick). The suspensions were left to stand for 1 hour before the pH was measured. Organic C and N ( $\text{C}_{\text{org}}$  and  $\text{N}_{\text{tot}}$ ) were measured by a C and N analyser (Carlo Erba Instruments, type C/N NA 1500 N) after we had dried the soil at 105 °C. For the determination of the water content, field-moist samples were dried at 105 °C until they reached constant weight. To measure total acid-soluble Fe and Pb concentrations the soil was digested in closed vessels (two replicates), following the procedure described

by Ilg et al. (2004). Ten ml of concentrated nitric acid was added to 2 g of field-moist soil. The vessels were heated to 180°C for 6 hours. After cooling, the digested samples were filtered (Schleicher and Schuell, diameter 150 mm, type 0790 ½, Reference No 10301645), transferred into 25 ml volumetric flasks, and subsequently each was filled to the mark with deionized water. The solution was analysed for Pb and Fe as described in the section 'analyses'.

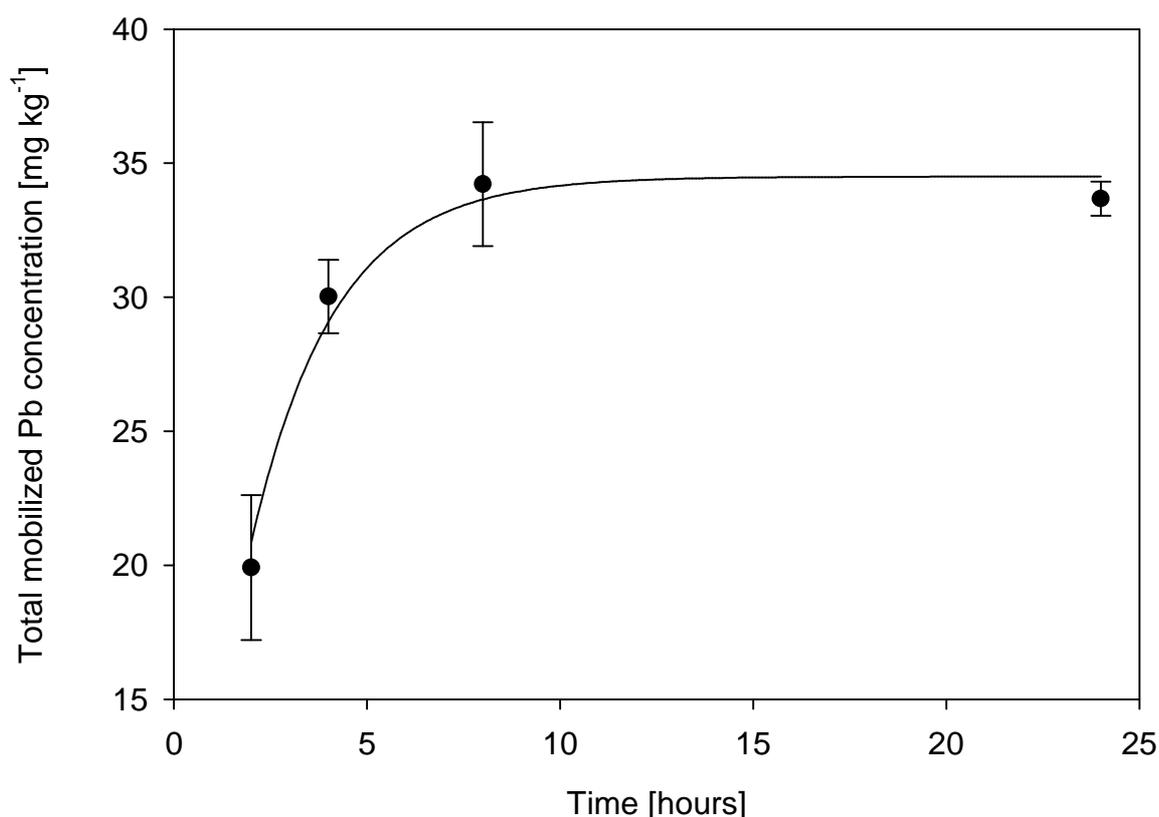
#### ***4.3.2 Dispersion experiments***

There are currently no standard methods for the determination of the stability of soil colloids. However, batch experiments are commonly used to determine the dispersibility and stability of colloids. They vary with respect to soil:water ratio and shaking time (Kaplan et al., 1996; Czigany et al., 2005). Batch studies by Miller and Baharuddin (1986) revealed that the percentage of clay that was dispersed by this method was strongly related to soil loss by surface run-off, indicating that this kind of experimental set-up relates to field observations.

We studied the mobilization of colloidal and dissolved Pb in batch experiments using field-moist samples (< 2 mm). Based on the results of preliminary experiments, we chose a soil:water ratio of 5 g field-moist soil to 50 g solution. This ratio proved to be wide enough to prevent an artificial generation of colloids by abrasion. At narrow soil:water ratio we observed a decrease in mean colloid size. This might be due to abrasion of mineral particles as has been suggested, for example by Curtin et al. (1995) for concentrated suspensions. Kinetic studies showed that equilibrium is reached after about 8 hours of shaking (figure 4.1). Therefore we used a shaking time of 12 hours on an end-over-end-shaker for our dispersion experiments.

Colloids are defined as particles sufficiently small to remain in suspension (Brady and Weil, 2002) and able to scatter light (Brezesinski and Mögel, 1993). Since particles greater than 1 nm and smaller than 1 µm show these properties, colloids have been defined as particles of that size range (Brady and Weil, 2002). However, these size limits are not uniformly defined in the literature. Scheffer and Schachtschabel (1998) characterize colloids to be of a maximum size of 2 µm. For

reasons of practicality, we chose a filter of a pore size of 1.2  $\mu\text{m}$  to separate dispersed colloids in the suspension of our batch system from coarser soil material. The used ultra-centrifugation technique allowed us to separate colloids of a size range between 4 and 10 nm from the suspensions (4 nm: organo-mineral colloids (averaged density  $d = 2.65 \text{ g cm}^3$ ); 10 nm: organic colloids (assumed density  $1.2 \text{ g cm}^3$ )).



**Figure 4.1:** Total mobilized Pb concentration as a function of shaking time (soil 1; pH of soil suspension: 3.9)

### **4.3.3 Effect of pH increase in the presence of a monovalent counterion**

To investigate the effect of increase in pH we adjusted the soil suspensions to pH 3, 4, 5, 6, ( $\pm 0.2$ ) and 7 ( $\pm 0.5$ ) with three replicates each. The pH was adjusted with 0.1 M KOH and 0.1 M HNO<sub>3</sub>. A monovalent base as opposed to a divalent was used to avoid the interference of Ca-specific coagulation and bridging effects with pH effects. To obtain pH 3 and 4 the required quantities of HNO<sub>3</sub> and KOH were added

at the beginning of the experiment. To obtain pH 5, KOH was added gradually during the first hour, and to obtain pH 6 and 7 KOH was added during the first 2 hours as the buffering of added hydroxide was slow. The ionic strength of the individual treatments was fixed at  $13.5 \pm 2.5$  mmol (pH 3 to 6), and  $15.5 \pm 3.0$  mmol (pH 7) with 0.2 M  $\text{KNO}_3$  solution.

#### ***4.3.4 Effect of pH increase – comparison of counterion valency***

For the comparison of a pH increase induced by a monovalent and divalent base we set up the following two series by adding either KOH or  $\text{Ca}(\text{OH})_2$ . We added 0.005 M  $\text{Ca}(\text{OH})_2$  and 0.05 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  solutions to adjust the pH to 3.9, 5.2, 5.8, and 6.9. Since the amount of dissolved  $\text{Ca}(\text{OH})_2$  added to the samples by the 0.005 M  $\text{Ca}(\text{OH})_2$  solution was not enough to obtain pH 5.2 and 5.8 in the suspensions we also added solid  $\text{Ca}(\text{OH})_2$ . We adjusted pH 6.9 by adding 0.005 M  $\text{Ca}(\text{OH})_2$  solution and solid  $\text{Ca}(\text{OH})_2$ . To illustrate an exemplary comparison with a monovalent base 3 series were adjusted for pH values 3.3, 4.8 and 6.3 by adding appropriate quantities of 0.1 M KOH and 0.1 M  $\text{KNO}_3$  solutions. The ionic strength of each individual batch of each treatment was kept constant by adding appropriate quantities of either 0.05 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  or 0.1 M  $\text{KNO}_3$  solution and amounted to  $46 \pm 16$  mM.

At the ends of both experiments, the pH was checked in the suspensions prior to filtration through a 1.2- $\mu\text{m}$  cellulose-nitrate-membrane (Sartorius, Type 11303 – 047N). An aliquot of the filtrate was acidified (to  $\text{pH} < 1$ ) with concentrated nitric acid for the measurement of the total Pb concentration in solution. In addition, we determined concentrations of total organic C. We investigated the effect of a pH-increase and for soil 1 we also measured optical density, particle size and zeta potential (see analytical methods below). An aliquot of the filtrate was ultracentrifuged at 300 000 g for 1 hour at 10 °C (Beckman Optima TL) to separate the colloids. The supernatant was transferred into Eppendorff plastic caps, acidified with nitric acid and analysed for concentrations of dissolved Pb and organic C. The difference of the Pb and C concentration between un-ultracentrifuged and ultracentrifuged samples accounts for colloidal fractions of Pb and C. At pH 5, 6 and

7, the colloidal residues were digested with concentrated nitric acid in closed vessels at 180° for 6 hours and subsequently analysed for Fe.

#### **4.3.5 Analyses**

Lead and Fe were measured with a flame atomic absorption spectrophotometer (Perkin Elmer 1100 B), at a wavelength of 217.0 nm for Pb and at 248.3 nm for Fe. Preliminary experiments showed no difference between results gained from acid-digested colloidal suspensions as described by the EPA method 3015 (EPA, 1994) and undigested suspensions. The concentration of organic C in the solutions was measured by a total organic carbon analyser (TOC – 5050 A, Shimadzu).

The optical density determined as light absorption at 525 nm was taken as a measure for the relative amount of dispersible particles as specified by Kretzschmar et al. (1997) on a spectrophotometer (Beckmann Instruments, DU 60 Series). At pH 3, 4 and 5 direct absorbance measurements were possible. However, at pH 6 and 7, samples were too concentrated, and dilution (with millipore water) was required. This dilution reduces the ionic strength and might thus have led to a disaggregation of larger particles. However, the smaller particles created still have an influence on the measured absorbance. We observed that colloid-free dissolved organic matter solution also absorbs light at 525 nm. To correct for the interfering absorbance of this material, the absorbance of ultracentrifuged, colloid-free samples was measured. This absorbance was subtracted from the absorbance of the un-centrifuged samples.

Particle sizes (average diameter) were determined by dynamic light scattering (HPPS – High Performance Particle Size, Malvern Instruments) at a wavelength of 633 nm and a scattering angle of 173° after previous calibration of the instrument with a standard of known particle size. Zeta potential was calculated based on the electrophoretic mobility of the colloids, which was analysed by a Zetasizer 2000 photon correlation spectrometer (Malvern Instruments).

At pH 5 and 7 we characterized the colloidal residue by scanning electron microscopy (SEM; Hitachi S-2700) coupled with an energy-dispersive analysis of X-rays (EDX; SAMx, software 'IDFix' - acquisition parameter of the beam: accelerating voltage: 20 kV, beam current: 500 nA). The suspension was applied to a glass support and the suspension of pH 7 additionally coated with C.

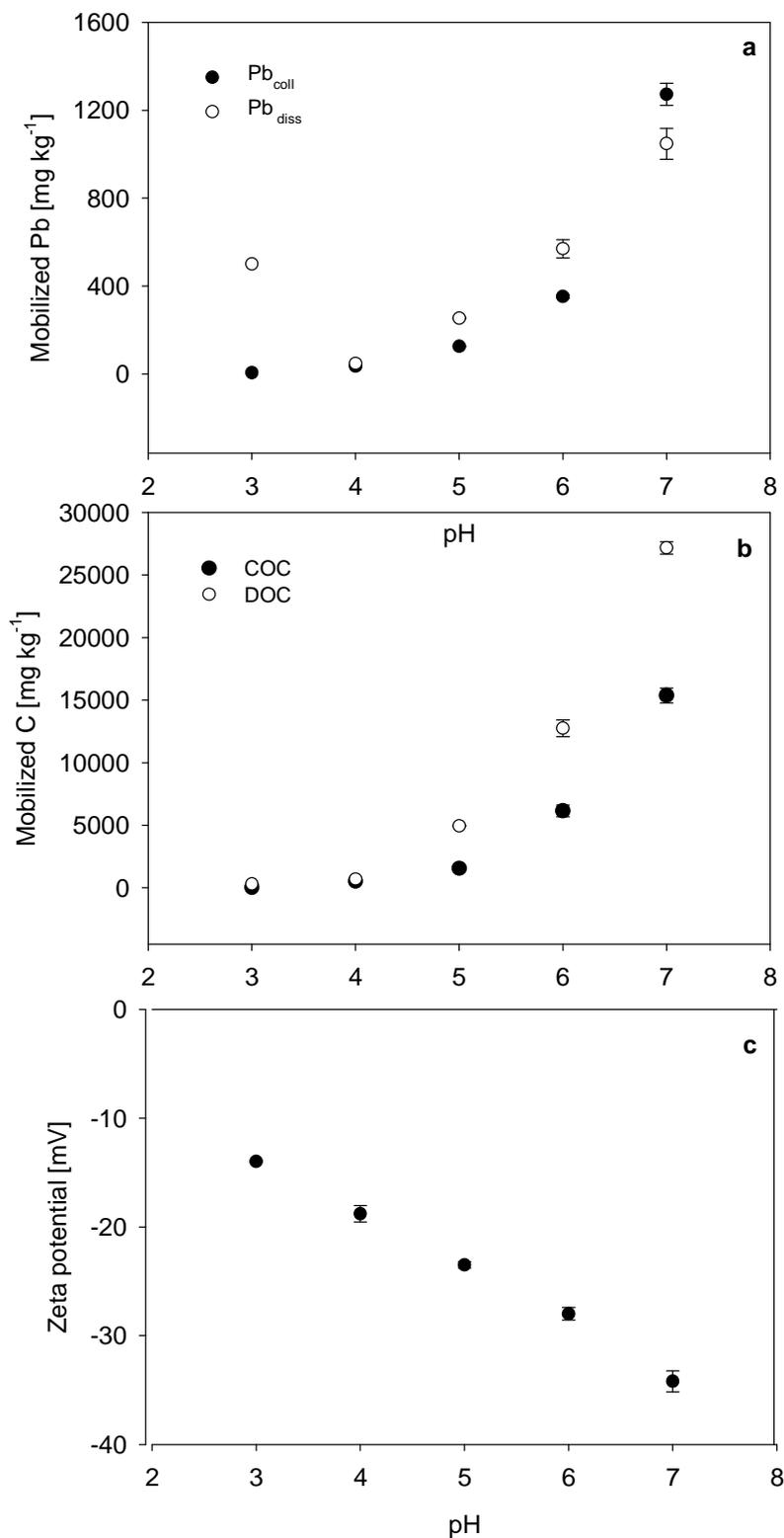
The data presented in the graphs is given as the average value of three replicates (soil 1) and two replicates (soil 2)  $\pm$  standard error.

## **4.4 Results and Discussion**

### ***4.4.1 Effect of a pH increase in the presence of a monovalent base***

#### *4.4.1.1 Effects of pH on Pb mobilization*

At pH 3, only dissolved Pb was detectable. The concentrations of dissolved Pb concentration reached a minimum at pH 4, followed by an increase with increasing pH (figure 4.2a). Because the solubility of dissolved organic matter increases with increasing pH (Jardine et al., 1989), the concentration of this matter increased (figure 4.2b) and was strongly correlated to dissolved Pb concentrations from pH 4 to pH 7. Various studies have shown DOM-induced Pb mobilization (e.g. Sauvé et al., 1998). However, the mobility minimum observed in our study was at lower pH than in other studies. Herms and Brümmer (1984) for example found least Pb mobility in topsoils in the pH range 5 to 6.



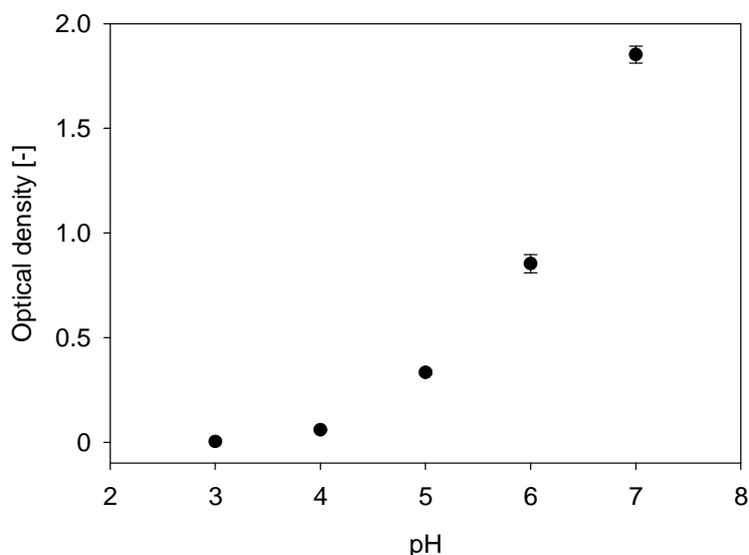
**Figure 4.2a-c:** Mobilized Pb (a), organic C (b), and zeta potential (c) of soil suspensions extracted from soil 1 at various pHs of the KOH treatment (after 1.2  $\mu$ m filtration).  $Pb_{coll}$ : colloidal Pb,  $Pb_{diss}$ : dissolved Pb, COC: colloidal organic carbon, DOC: dissolved organic carbon.

The strong mobilization of Pb even at pH 5 from our soil samples might be due to the large concentration of organic matter in the soil. At pH 3 and 4 concentrations of extractable C were in the range given for the concentration of dissolved organic C in soil solution of acid forest soils (10-90 mg C l<sup>-1</sup>, Kalbitz et al., 2000), and were about 10 times larger at pH 7. The very large concentration of dissolved organic C especially at higher pH can be explained by the use of a monovalent base (KOH) as opposed to the divalent Ca(OH)<sub>2</sub> to increase the pH in our experiment. Such large concentrations will not be found under 'natural' conditions, but may occur after application of alkaline fertilizers or after clear cutting.

The results demonstrated a continuous increase of the colloidal Pb fraction in the pH range from almost zero at pH 3 to 1200 mg kg<sup>-1</sup> at pH 7 (figure 4.2a). At pH 4, 36 % of extractable Pb and 34 % of extractable C were bound to colloids. Our results accord with those from Wang and Benoit (1996), who found that 50 % of Pb in soil solutions from OA horizons of the Hubbard Brook experimental site (pH 4 to 4.7) were bound to colloids. Thus humic rich forest topsoils may pose exceptional risk of colloid mobilization, and much larger than in arable soils at pH above 6 (e.g. Kaplan et al., 1997), which have been used in previous studies.

At pH 7 colloidal Pb was the dominant species (approximately 70 % of total extractable Pb). The increase of colloid mobilization with increasing pH is a well known phenomenon. Increasing surface charge as observed in our study from zeta potential measurements (figure 4.2c) enhances colloid mobilization and stability (e.g. Kaplan et al., 1997).

Colloidal Pb concentrations increased with increasing optical density of the suspensions (figure 4.3). These results indicate that the increase in colloidal Pb was caused mainly by stronger particle dispersion at high pH and less likely by a greater affinity of Pb for colloids.



**Figure 4.3** Optical density of soil suspensions extracted from soil 1 at various pHs of the KOH treatment (after 1.2  $\mu\text{m}$  filtration)

### 4.4.1.2 Effects of pH on colloid properties

Two EDX spectra of colloids at pH 7 and 4 are shown as examples in figure 4.4a and b. They are representative for the colloids dispersed at the individual pH. At pH 7 we detected Al, Si, O, K and Pb as the main components of dispersible colloids (figure 4.4a). Lead might be associated with aluminosilicates, which are part of the colloidal fraction as proposed by Kaplan et al. (1997). In addition, the strong correlation between concentrations of colloidal Fe and concentrations of colloidal Pb (pH 5 to 7,  $r = 0.99$ ; data not shown) indicates that Fe is a further component of the colloids. At pH 4, the comparatively small intensity of the Al signal together with the very high C and O peaks indicate the presence of organic Pb-containing colloids (figure 4.5). The SEM/EDX analyses confirm the presence of different types of colloids at pH 4 and 7. However, increasing concentrations of colloidal organic C (figure 4.2b) were significantly correlated with colloidal Pb concentrations. This observation allows for the assumption of organic C being a component of the colloids across the entire pH range measured.

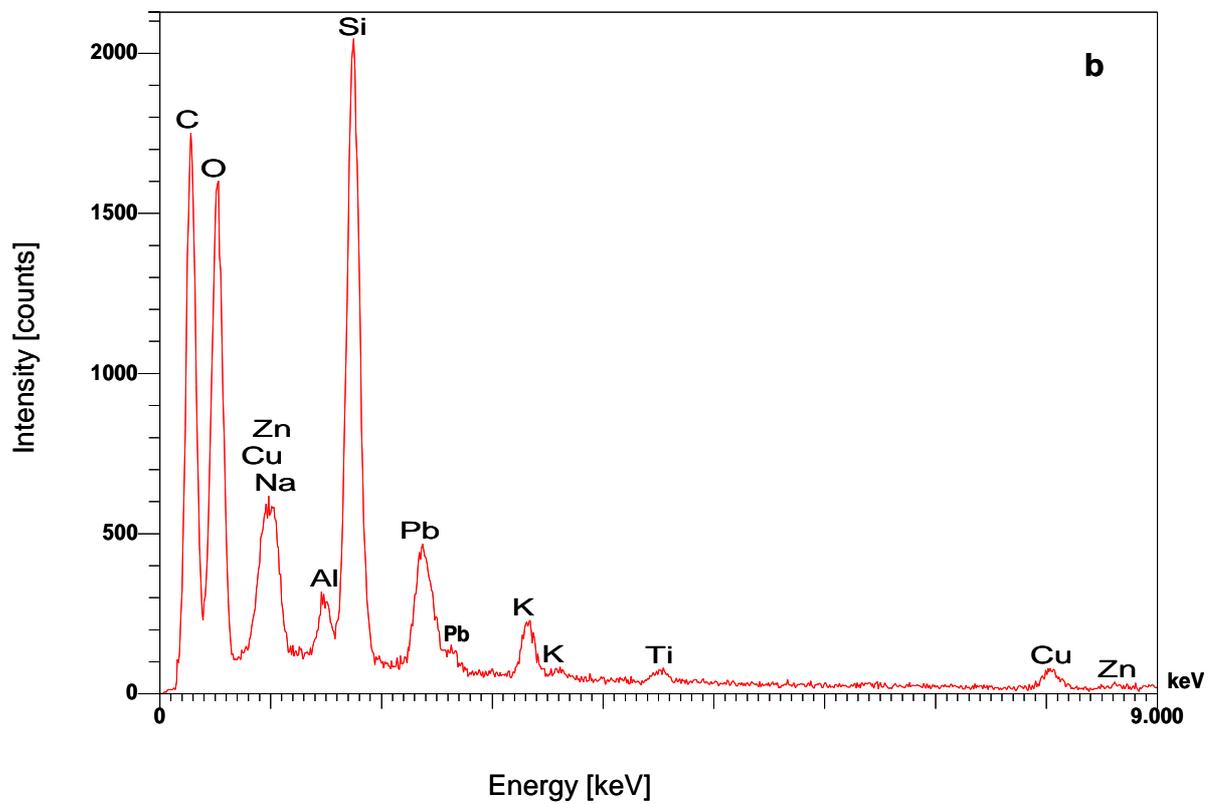
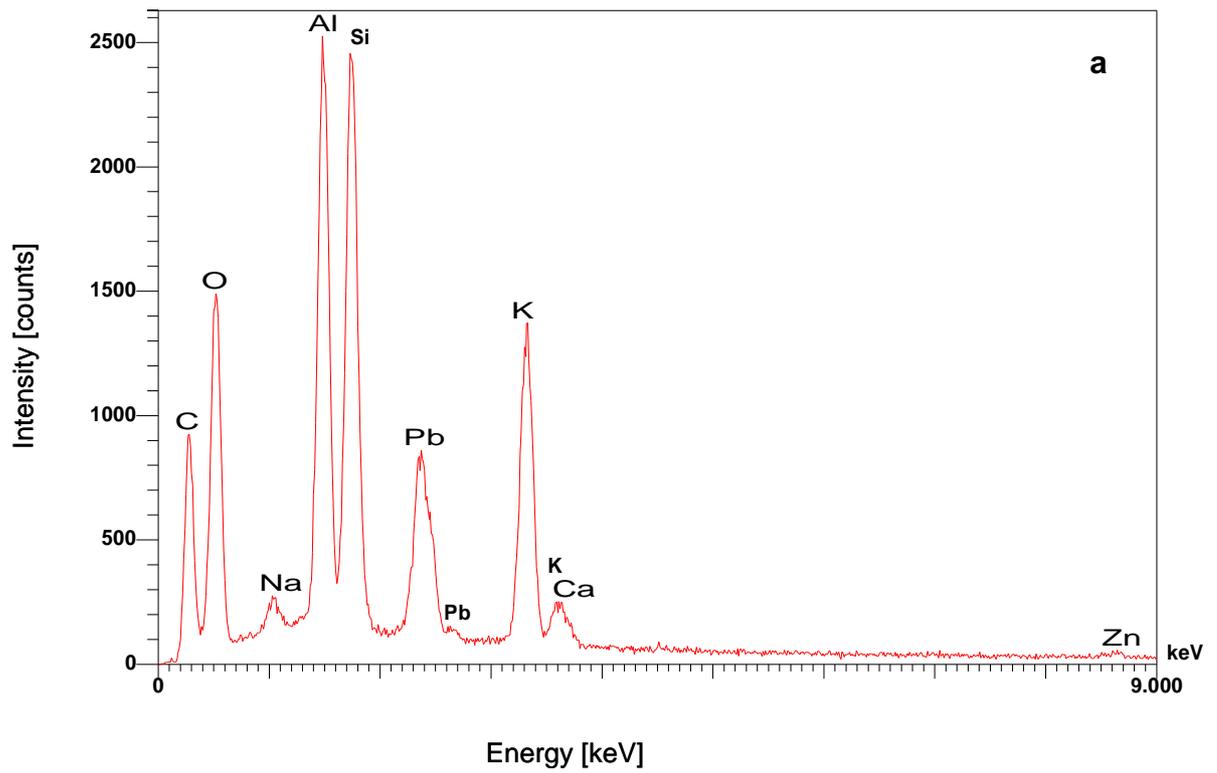
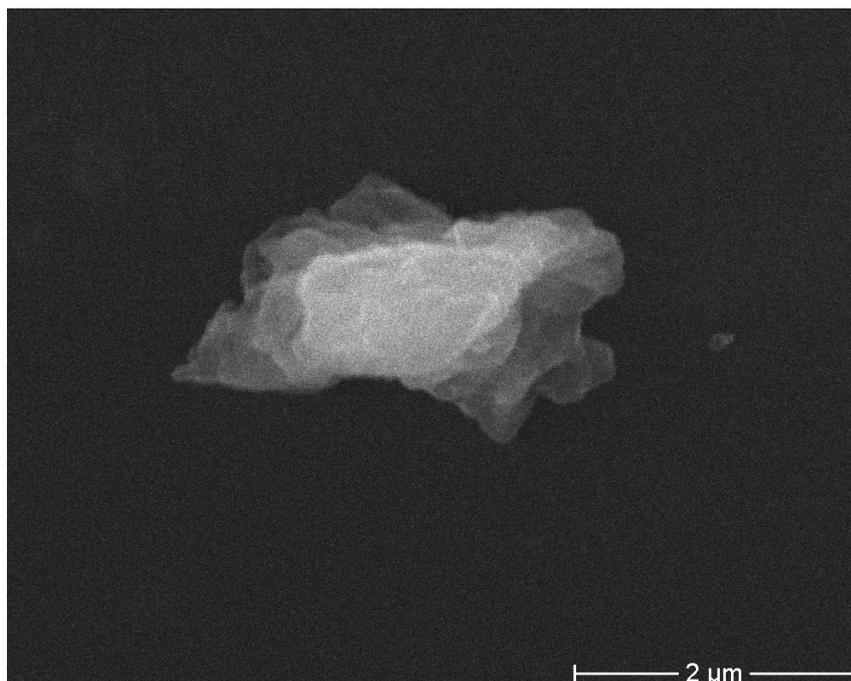


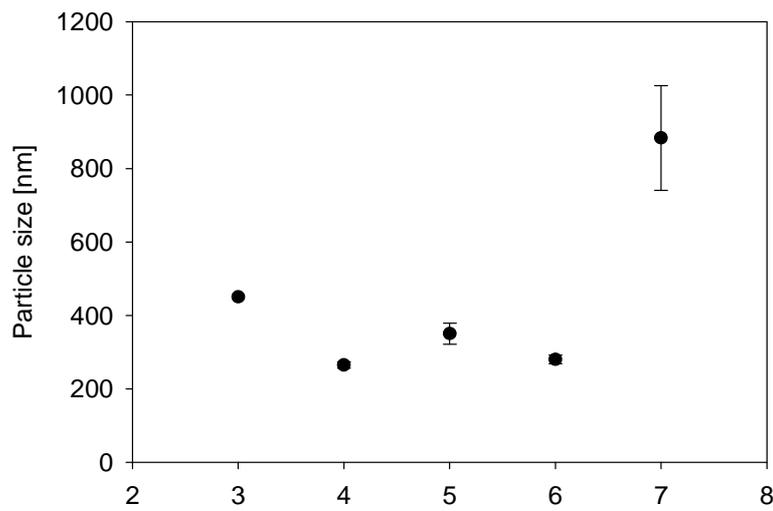
Figure 4.4a+b: EDX spectra of colloids dispersed at (a) pH 7 and (b) pH 4 of soil 1 (KOH treatment)



**Figure 4.5:** SEM image of colloids dispersed at pH 4 (soil 1, KOH treatment)

Soil minerals mobilized by changes in charge and stabilized by organic coatings might be the form of colloids mobilized at pH 6 and 7, whereas organic macromolecules or metal-organic precipitates, which have been suggested to occur in acid soils (e.g. Nätscher and Schwertmann, 1991; Fotovat et al., 1997) might be the colloids mobilized in the low pH range. At pH 6, larger concentrations of colloidal Fe suggest the presence of colloidal Fe oxides or colloidal Fe-organic-complexes (Jones et al., 1993). Above a certain ratio of Pb to dissolved organic matter Pb might no longer be soluble and may be present in colloidal form as shown by Lang et al. (2005). Remarkably, the ratio of Pb to dissolved organic C ( $50 \mu\text{g Pb g}^{-1} \text{C} \pm 12$ ) is significantly less than the Pb loading of colloidal organic C ( $82 \mu\text{g Pb g}^{-1} \text{C} \pm 9$ ). This hypothesis that metal organic salts are the colloids in acid soils accords with the observations from Hill and Aplin (2001) who compared the colloids of rivers draining carbonate and silicate terrains. They concluded from their results that organic macromolecules and associated metals, which were mobilized in soils by weathering induced by acid and dissolved organic matter, form the prevailing colloids of the low-pH acid silicate terrains. Similarly, our findings accord with the results of Saar and Weber (1980) who observed the formation of insoluble  $\text{Pb}^{2+}$ -fulvic acid complexes at a very small ratio of  $\text{Pb}^{2+}$  to fulvic acid.

From pH 3 to 6 the mean particle size remained almost constant, whereas we found larger particles at pH 7 (figure 4.6). This is accords with the hypothesis of different colloid composition at different pH. Kaplan et al. (1993) found that large colloids (750 nm) consist mainly of quartz and clay minerals. Humic-rich colloids sampled from surface bogwaters were mostly smaller than 220 nm (Huynh and Jenkins, 2001).



**Figure 4.6:** Size of mobilized colloids of soil 1 at various pHs of the KOH treatment (after 1.2  $\mu\text{m}$  filtration)

The particle charge increased continuously with increasing pH (figure 4.2c), obviously being one reason for colloid mobilization. Given the proposed differences in colloid composition with increasing pH, we think that the pH-zeta potential relation is similar for different types of colloids.

### 4.4.1.3 Mechanisms of colloid mobilization

Compared with data in the literature our results show a strong mobilization potential of colloidal Pb, even at low pH. The increasing Pb mobilization with increasing pH and surface charge of the colloids clearly showed that electrostatic stabilization is one of the reasons for colloid mobilization in the soil. Organic matter might act as coating around inorganic particles, and as suggested by Kaplan et al. (1996), might mask the surface charge of the underlying mineral and lead to more negative values.

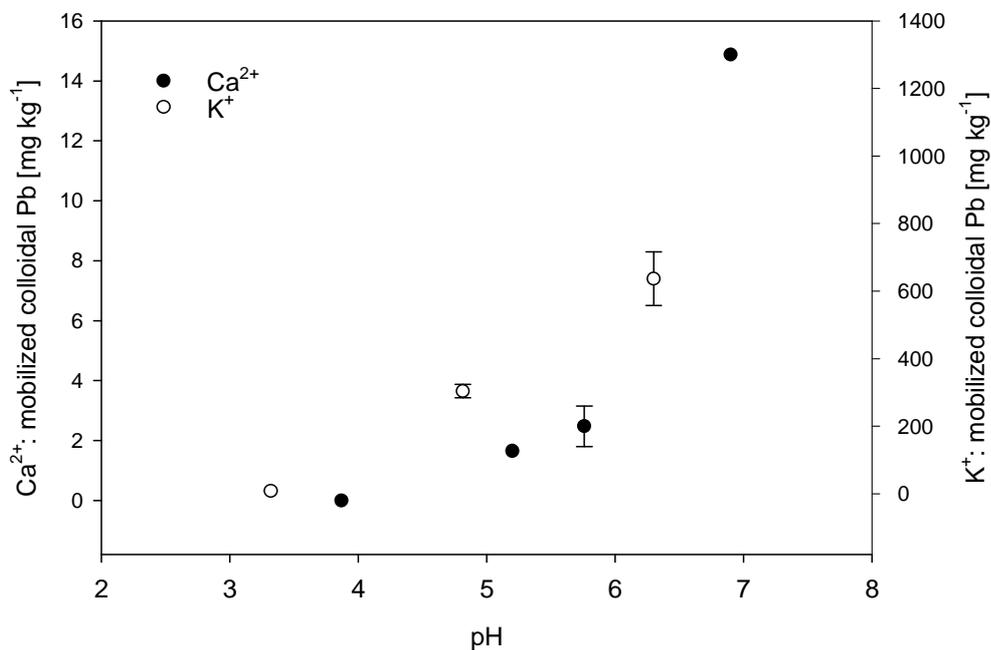
However, the zeta potential measured in our study was not extraordinarily large. Kaplan et al. (1993) found values from -32 to -44 mV for mobile colloids (we found -14 to -34 mV). This implies that surface charge might not be the only reason for colloid mobilization in our case.

Kaplan et al. (1997) suggested that organic coatings prevent inorganic particles from aggregating not only by electrostatic but also by steric repulsion. Similar observations were reported by Heil and Sposito (1993) who postulated that electrostatic and steric properties reduce the van-der-Waals-forces between particles and thus lead to an enhanced colloidal stability. Kretzschmar et al. (1993) reported the steric stabilization effect of clay colloids to be affected by the macromolecular configuration of humic substances that changes with the proton concentration. These steric effects might be important for our soil because of the large concentration of organic matter and may mobilize colloids even at low pHs. In agreement, Burba and van Bergh (2002) found surprisingly stable humic-rich colloids in acid bogwater samples (pH 3.5 – 4.5). Thus, the classical model of colloid mobilization and stability might underestimate the risk of colloid mobilization at the boundary between forest floor and mineral horizons and might be extended for organic horizons by inclusion of steric stabilizing effects.

#### **4.4.2 Effect of pH increase – comparison of counterion valency**

The comparison of an increase in pH on the dispersibility of colloidal Pb showed a much stronger mobilization in the presence of the monovalent  $K^+$  than in the presence of the divalent  $Ca^{2+}$  (figure 4.7a). Whereas in the KOH treatment, the concentration of colloidal Pb showed a strong and uniform increase, in the presence of  $Ca^{2+}$  the pH-induced mobilization of colloidal Pb was much less distinct. The very strong 7-fold increase occurred only at  $pH > 5.8$ . This pronounced increase in concentration of colloidal Pb, which goes along with a similarly pronounced increase in colloidal organic C (data not shown), accords with the following conceptual model explaining the role of particle charge in colloid mobilization: at low pH (i.e. little deprotonation) the bridging effect of the  $Ca^{2+}$  masks the increasing charge effect, as described by Schäfer et al. (2000), and therefore leads to an immobilization of

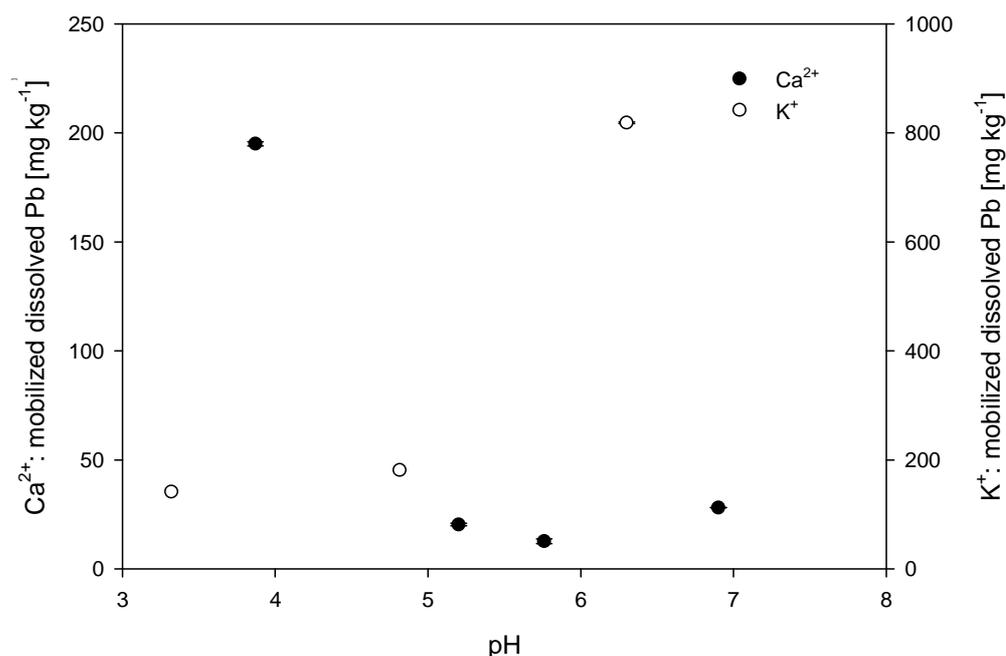
colloids, as observed by Dahlgren and Marrett (1991), i. e. no colloidal Pb or only very small concentrations. With increasing pH, and the resulting greater degree of deprotonation of functional groups, the increasing forces of electrostatic repulsion can no longer be fully compensated by Ca bridging. This is the onset of a strong pH-induced mobilisation of colloids. In addition to this model assumption, the dispersion of  $\text{Pb}(\text{OH})_2$  at pH 6.9 could occur. Even though concentrations of dissolved Pb exceed the solubility product and therefore indicate complexation of Pb by dissolved organic C, the dispersion of precipitated  $\text{Pb}(\text{OH})_2$  cannot be excluded.



**Figure 4.7a:** Concentrations of colloidal Pb of soil suspensions extracted from soil 2 at various pHs by KOH and  $\text{Ca}(\text{OH})_2$  (after 1.2  $\mu\text{m}$  filtration)

Whereas concentrations of dissolved Pb increased with increasing pH in the KOH treatment, they decreased in the  $\text{Ca}(\text{OH})_2$  treatment to a minimum at pH 5.8, after which concentrations slightly increased again (figure 4.7b). This observation may be explained by a combination of both charge and ‘bridging’ effect, i.e. the interaction of the cation with dissolved organic C. In the KOH treatment, the mobilization of dissolved organic C increased with increasing pH as a result of the deprotonation of functional groups. There are no ‘bridging’ interactions between the monovalent  $\text{K}^+$ -ion and dissolved organic C, and thus allows a high degree of complexation of  $\text{Pb}^{2+}$  with dissolved organic C. In the  $\text{Ca}(\text{OH})_2$  treatment, however, the pH-induced mobilization of dissolved organic C is reduced by the divalent  $\text{Ca}^{2+}$ , which ‘bridges’

between negatively charged molecules of dissolved organic C (Dahlgren and Marrett, 1991), leading to the formation of precipitates of Ca and organic C. These precipitates may in part be present as colloids in our filtrate. Thus, less dissolved organic C is available to complex Pb and therefore Pb precipitates, resulting in a minimum of dissolved Pb concentrations at pH 5.8. However, at pH exceeding 5.8, the increasing concentration of mobilized dissolved organic C is no longer masked by  $\text{Ca}^{2+}$ . Therefore, dissolved organic C molecules are then available to complex Pb and lead to an increased mobilization of dissolved Pb. Concentrations of dissolved Pb of the  $\text{Ca}(\text{OH})_2$  treatment exceed those of the KOH treatment between pH 3 and 4. Considering the comparatively high Ca concentration in solution, we think that this is an additional displacement of Pb from exchange sites, resulting in concentrations of Pb greater than those in the KOH treatment.



**Figure 4.7b:** Concentrations of dissolved Pb of soil suspensions extracted from soil 2 at various pHs by KOH and  $\text{Ca}(\text{OH})_2$  (after 1.2  $\mu\text{m}$  filtration)

#### 4.5 Environmental Relevance

The batch experiments determine the dispersibility and quality of colloids under the described physico-chemical conditions and give an indication on the effect of increasing pH. However, these results might not be translated directly to the field scale when the effects of liming are evaluated. They do not allow for a derivation of absolute concentrations in the soil solution under field conditions. However, our results indicate a high risk of mobilization of colloidal Pb at the site we studied. We conclude that in acid forest soils with organic layers large amounts of colloids may be mobilized, especially at the boundary between organic and mineral horizons. At low pH organic colloids seem to be of particular relevance. These colloids may in part consist of metal-organic salts, may be stabilized by steric effects and might be much more stable than colloids in soils containing less organic carbon. Even though the presence of  $\text{Ca}^{2+}$  strongly reduces the concentration of colloidal Pb in comparison with  $\text{K}^+$ , our findings show that there is a risk that both colloidal and dissolved Pb increase at a pH value above 5.8. Therefore, the danger of Pb leaching not only in dissolved, but also in colloidal form should be taken into account in the risk assessment of limed sites. Further studies are needed to assess whether the colloids remain mobile in the subsoil.



# 5 Lead, Antimony and Arsenic in dissolved and colloidal Fractions from an amended Shooting Range Soil as characterized by Multi-stage Tangential Ultrafiltration and Centrifugation

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## 5.1 Abstract

Size and composition of colloids determine their relevance as carriers of heavy metals in soils. Liming may alter these characteristics of colloids. In batch studies, we compared the influence of increasing pH and cation valency on the mobilization of soluble and colloid-associated Pb, As and Sb by adding Ca(OH)<sub>2</sub> and KOH to soil samples of a contaminated shooting range site. Multi-stage tangential ultrafiltration and centrifugation were used for the size fractionation of colloids in suspensions. Whereas the monovalent K-ion induced the dispersion of smaller (100 kDa – 220 nm) organo(-mineral) colloids, the divalent Ca-ion suppressed the dispersion of the latter and led to the formation of larger colloids (220 – 1200 μm), presumably “bridging”-products between Ca, Pb and DOM. Whilst both techniques inherit shortcomings such as problems with build-up on membranes (filtration) and incomplete size fractionation of colloids with varying density (centrifugation) the combination of both allows for (i) an estimate of colloids mainly composed of mineral material and colloids consisting mainly of organic matter as well as (ii) the differentiation between “free” colloidal organic C and organic C associated with mineral colloids of different size classes.

## **5.2 Introduction**

Colloids, which are particles of a diameter  $< 1 \mu\text{m}$  (Ranville et al., 2005) play a crucial role in the movement of contaminants in the environment. These colloidal particles can consist of clay minerals, iron (Fe)-, aluminium (Al)- and manganese (Mn)-oxides as well as –hydroxides, organic macromolecules and microorganisms such as viruses and bacteria (Brady and Weil, 2002). Each type may vary in their response to physico-chemical changes in the environment. The large specific surface to volume ratio enables colloids to sorb large quantities of organic and inorganic pollutants (Kretzschmar et al., 1999). Their transport and deposition behaviour is not only controlled by their physico-chemical properties such as surface chemistry and composition, but also by the size and shape of the colloids (Ranville et al., 1999). The size fractionation of soil colloids together with their characterization may help to identify their composition. This information may thus allow for a better understanding and prediction of their role as carriers of different pollutants (Buffle and Leppard, 1995).

### ***5.2.1 Separation methods for the size fractionation of colloids***

Several techniques such as centrifugation, ultrafiltration, and field-flow fractionation (FFF) have been applied to separate or fractionate colloidal particles in soil suspensions (Buffle and Leppard, 1995). As opposed to FFF, ultrafiltration and centrifugation are techniques which do not cause a change in sample equilibrium (Nifant'eva et al., 2001). This is crucial in work on colloid chemistry. While centrifugation techniques can introduce errors in particle size fractionations through differences in particle densities (e. g. due to the presence of organic matter; Wu et al., 2003) common ultrafiltration techniques also inherit a few shortcomings such as (I) adsorption of macromolecules on the membranes and (II) the aggregation of smaller colloids to larger colloids at the membrane surface due to the formation of a thick diffusive layer induced by the filtration process (Buffle and Leppard, 1995). In addition a drawback associated with every filtration process is the artefact which may be caused by non-spherical particles larger than the pore size of membranes. The concept of multi-stage tangential ultrafiltration (MTUF), however, addresses these two mentioned limitations: Adsorption of macromolecules can be overcome by

the use of specially selected filter discs. Coagulation can be minimized by filtering the sample over filters with successively decreasing pore size, by applying a tangential flow and a very low flow rate of the cross flow to minimize the diffusive layer (Buffle and Leppard, 1995). Multi-stage tangential ultrafiltration has been applied with success in freshwater systems to understand the size distribution of aquatic humic substances (Burba et al., 1998) as well as the association of heavy metals (Buykx et al., 2000) and organic compounds (Gadel et al., 2000) with particulate or colloidal matter. However, no work has yet been carried out on soil suspensions. Depending on the texture and the physico-chemical properties of the soil matrix, soil solution may contain higher concentrations of dissolved and colloidal species than aquatic water samples rendering the filtration process more difficult. The MTUF system can be modified for the separation of natural colloidal material in soil solutions to prevent changes in sample ionic strength through the re-circulation of the < 100kDa filtrate (defined as “dissolved”) as described by Buykx et al. (2000). Considering the strong influence of ionic strength on soil colloid stability, this technique of a closed system loop presents a powerful method to separate colloids by means of multi-stage tangential ultrafiltration. The aim of our work is to apply the modified MTUF system to the separation of soil extracts and to compare the results produced by MTUF and centrifugation.

### ***5.2.2 The impact of liming on shooting range sites***

On shooting range sites, where the metals of main concern are lead (Pb), arsenic (As) and antimony (Sb), the colloid-facilitated transport of contaminants may be relevant. Whilst numerous publications show that colloids are a major pathway for Pb in soils (Jensen et al., 1999, Egli et al., 1999; Denaix et al., 2001) detailed studies for colloid-associated As and Sb are missing. However, considering the high affinity of As (Kabata-Pendias & Pendias, 2001) and Sb (Tighe et al., 2005, Lintschinger et al., 1998) to Al- and Fe-oxides one may derive colloid-associated mobilization of these two elements to be a relevant process in soils. Despite the recognition of the sorption capacity for metals and the translocation potential of colloids, risk assessment studies often do not differentiate between colloid-associated and dissolved metals.

The application of lime is a common technique suggested for the remediation of contaminants at shooting range sites (EPA, 2001). The increase in soil pH due to the addition of lime has been shown to increase the retention of Pb in soils (McBride, 1994). Although hardly investigated, liming might have a significant effect on the generation and stability of colloids. In fact, the release of colloids in soils is controlled by the physico-chemical properties of the soil solution, with pH (Kaplan et al., 1996) and dissolved organic matter (DOM) concentration (Kretzschmar et al., 1999) playing a key role in governing colloid stability. Liming has a number of effects on these parameters governing the mobilization of both soluble and colloid-associated metals:

- a) pH increase
- b) addition of  $\text{Ca}^{2+}$  ions into the soil

Colloid stability is enhanced at elevated pH due to increasing negative particle charge (Kretzschmar et al., 1999). In addition, the increase in pH induces a mobilization of dissolved organic C which may lead to the formation of organic surface coatings on minerals. These coatings are reported to enhance colloid stability (Kaplan et al., 1997).

Beside the possible generation of colloids such as Ca-arsenate (Sadiq, 1997) and “bridging” products between Ca and DOM (Dahlgreen and Maret, 1991) the addition of the  $\text{Ca}^{2+}$  ion has a destabilizing effect on colloids. The higher valency of the  $\text{Ca}^{2+}$  ion leads to a compression or even collapse of the diffusive double layer (McBride, 1994), facilitating particle aggregation. In addition, Kretzschmar and Sticher (1997) observed the stabilizing effect of organic coatings to be reduced by increasing Ca concentrations, which may be due to a bridging effect of the bivalent Ca.

The resulting net effect of the stabilizing pH-effect and the destabilizing Ca-effect, however, is unknown.

### **5.2.3 Aim and scope of the work**

Results of Klitzke et al. (in press) showed that an increasing pH leads to the mobilization of Pb-bearing colloids and to a change in composition of the mobilized colloids. These observations are followed up by the size fractionation of the colloids in the presented study. The aim of the paper is (I) to investigate the impact of liming on soil solution and colloid chemistry and (II) to compare the results produced by MTUF and centrifugation by testing the following hypothesis:

1. MTUF is a powerful tool for the fractionation of soil colloids and has a better applicability than centrifugation.
2. Increasing pH enhances the mobilization of colloidal Pb, As and Sb
3. The addition of  $\text{Ca}^{2+}$  reduces this pH-effect
4. Both a change in pH and valency of the counterion impact on the quality and size distribution of colloids.

## 5.3 Material and Methods

### 5.3.1 Soil collection and characterization

The study soil was collected from the  $A_h$ -horizon of a former shooting range location in Lüerdissen, North Rhine-Westphalia, Germany, classified (according to World Reference Base) as Cambisol with a texture of loamy silt. The soil was air-dried, homogenized, sieved < 2 mm and stored in plastic-bags at room temperature until further analysis. The soil pH and electrical conductivity were determined in 1:2.5 (mass to volume) soil suspensions using deionised water (Millipore; WTW inoLab). The water content was determined on field-moist samples dried to a constant mass at 105°C. Total organic C and N ( $C_{org}$ ,  $N_{org}$ ) were determined on soil dried at 105 °C using a C/N-analyzer (Elementar, vario MAX CN Elemental Analyzer). The determined soil-chemical characteristics are presented in table 5.1. Total trace metal concentrations in the < 2 mm soil sample were determined in duplicate using a microwave-assisted acid digestion procedure (0.25 air-dried soil, 5 mL aqua regia) and inductively coupled plasma - optical emission spectroscopy (SpectroFlame, Spectro Analytical Instruments) and hydride generation - atomic absorption spectroscopy for As and Sb (GBC 906AA). Oxalate-extractable Fe and Al were determined by adding 100 mL of ammoniumoxalate/oxalic acid solution to 5 g of air-dried soil. The mixture was shaken for 2 hours and subsequently filtered over a folded filter. The obtained filtrates were analyzed by flame atomic absorption spectroscopy (Perkin Elmer 1100 B) at wavelengths of 309.3 nm (Al) and 248.3 nm (Fe). Total metal and oxalate-extractable concentrations in the soil are presented in table 5.1.

**Table 5.1:** Some physico-chemical parameters, total heavy metal and oxalate-extractable Fe ( $Fe_{ox}$ ) and Al ( $Al_{ox}$ ) concentrations [ $mg\ kg^{-1}$ ] of the used soil, determined as duplicate

pH <sub>H2O</sub>		Conductivity [ $\mu S\ cm^{-1}$ ]		C/N ratio [-]		C <sub>org</sub> [%]		N <sub>tot</sub> [%]			
5.0		53.1		17.7		8.9		0.5			
Pb	As	Sb	Al	Al <sub>ox</sub>	Fe	Fe <sub>ox</sub>	Mn	Ca	Mg	K	P
8 844	70	122	12 118	1 956	10 642	3236	143	1 854	1 792	2 816	694

### **5.3.2 Soil batch extractions**

The < 2 mm soil sample was incubated at 60% water holding capacity for at least 1 week (max. 3 weeks) prior to extractions. Soil suspensions were prepared at a soil to solution ratio of 1:10 (5 g incubated soil: 50 mL solution). The sample treatments were prepared in duplicate by adjusting soil suspension pH's to  $6.5 \pm 0.1$  using 0.01 M KOH or 0.009 M (saturated)  $\text{Ca}(\text{OH})_2$  solutions. Differences in ionic strengths between KOH and  $\text{Ca}(\text{OH})_2$  treatments were compensated for by the addition of 0.01 M  $\text{KNO}_3$  solution as a background electrolyte to KOH suspensions. A control treatment was used to compare pH changes from the original pH values in soil suspensions through the addition of 0.01 M  $\text{KNO}_3$  background electrolyte without pH adjustment. Soil suspensions were shaken on an end-over-end shaker for 16 h (10 rpm) and filtered to < 1.2  $\mu\text{m}$  (cellulose-nitrate; Sartorius) prior to colloid fractionation.

### **5.3.3 Colloid fractionation - membrane filtration**

A modified multi-stage tangential ultrafiltration system was developed based on an instrument previously outlined by Burba *et al.* (1995). The MTUF system consisted of four chambers of 25 mm radius (~ 2 - 3 ml volume) made from a Perspex (high purity acrylic polymer) material. This system has a smaller total solution volume and a slightly larger filtration area/volume than the original one designed by Burba *et al.* (1995). This translated in a shorter time required for equilibration (see below) and the system could cope better with solution having higher concentrations of organic and inorganic colloids (soil extracts) as compared to freshwater samples. The individual chambers were inserted with individual membrane filters of the following pore sizes: 0.45  $\mu\text{m}$  (mixed-cellulose-ester; Millipore), 0.22  $\mu\text{m}$  (mixed-cellulose-ester; Millipore), 0.1  $\mu\text{m}$  (polycarbonate; Whatman), and 100 kDa (polyethersulfone; Omega, Pall Gellman). The individual MTUF chambers were stacked with filters of decreasing pore size to allow for the sequential filtration of the < 1.2  $\mu\text{m}$  soil suspensions. The soil suspensions were circulated in the MTUF system using a liquid chromatography pump (Dionex) at a flow rate of 0.1 ml min<sup>-1</sup>. To prevent the build-up of colloidal material at filter membrane surfaces, a tangential flow rate of 3 ml min<sup>-1</sup> was applied to each chamber using Tygon tubing (inner diameter 1.3 mm)

and a peristaltic pump. The  $< 1.2 \mu\text{m}$  soil suspensions were separated into the following colloidal fractions:  $1.2 - 0.45 \mu\text{m}$ ,  $0.45 - 0.22 \mu\text{m}$ ,  $0.22 - 0.1 \mu\text{m}$ ,  $0.1 \mu\text{m} - 100 \text{ kDa}$ , and  $< 100 \text{ kDa}$ , with the filtrate passing through the  $100 \text{ kDa}$  membrane operationally defined in this study as the “dissolved”.

The MTUF system was cleaned before analysis by soaking in  $1 \%$   $\text{HNO}_3$  for  $12 \text{ h}$  and thoroughly rinsed with deionised water (Millipore). MTUF system tubing and O-rings were rinsed with  $1 \%$   $\text{HNO}_3$  and deionised water. Prior to the size fractionation of the sample the liquid chromatography pump was cleaned to remove potential trace metal and organic C contamination by flushing with  $30 \%$  isopropyl alcohol,  $0.1 \%$   $\text{HNO}_3$  and deionised water (Millipore). In order to prevent any release of organic C into the suspensions, the membrane filters were prepared by soaking in  $0.1 \text{ M NaOH}$  for  $1.5 \text{ h}$ , rinsing with deionised water and stored in  $0.5 \text{ M HNO}_3$  until analysis. The individual membranes were flushed with  $50 \text{ ml}$  deionised water (Millipore) prior to MTUF separations. MTUF system blanks using deionised water found trace metal and organic C concentrations below instrumental detection limits (Agilent 7500c ICPMS,  $0.2\text{-}0.5 \mu\text{g l}^{-1}$  and Skalar C/N Analyser;  $0.5 \text{ mg l}^{-1}$ ).

After the MTUF system was filled with solution and air bubbles removed from chambers approximately  $5$  to  $10 \text{ mL}$  of the “dissolved”  $< 100 \text{ kDa}$  filtrate was re-circulated to the sample chamber ( $1^{\text{st}}$  chamber,  $0.45 \mu\text{m}$  filter) at a flow rate of  $0.1 \text{ ml min}^{-1}$ . The re-circulation of the “dissolved” fraction is essential for the complete separation of colloidal material through all chambers (Buykx et al., 2000). This avoids the addition of external solutions as described by (Burba et al., 1998) that can affect the ionic strength of samples. At the end of this equilibration period (minimum  $9 \text{ h}$  as determined by breakthrough experiments, data not shown) the individual chambers were emptied and the solutions analysed for pH, electrical conductivity, organic C, and trace metal (i.e. As, Sb, Pb, Fe, Mn and Al) concentrations. Dissolved concentrations were subtracted from total concentrations in the individual chambers in order to determine the colloidal trace metal and organic carbon concentrations for each size fraction. In order to determine possible trace metal losses to filters at the completion of MTUF separations the individual membranes were microwave - assisted acid digested using  $5 \text{ ml}$  of concentrated  $\text{HNO}_3$  and analyzed for total As,

Sb, Pb, Fe, and Mn by inductively coupled plasma-mass spectrometry (Agilent 7500c). Recovery rates were calculated by summing up the individual element content of the suspensions of the individual size fractions and – if need be – their corresponding filter membranes. The sum was compared with the quantity initially introduced into the system (set to 100 %).

#### **5.3.4 Colloid fractionation - centrifugation**

A centrifugation technique was used to compare colloidal size fractions in soil suspensions determined by MTUF. The centrifugation cut-offs were selected according to MTUF membrane filter sizes: 0.45  $\mu\text{m}$ , 0.22  $\mu\text{m}$ , 0.1  $\mu\text{m}$ , and 100 kDa ( $\sim 9$  nm). A subsample (15 ml) of the  $< 1.2$   $\mu\text{m}$  soil suspensions was centrifuged at times calculated based on an averaged particle density of  $2.65$   $\text{g cm}^{-3}$  using the modified Stokes' equation described by Tanner and Jackson (1947). At completion of centrifugation the supernatant was removed into separate plastic vessels. An aliquot was acidified with 10  $\mu\text{l}$  of 7 M  $\text{HNO}_3$ . The acidified samples were analyzed for Pb (flame atomic absorption spectrophotometry, Perkin Elmer 1100 B), Fe (graphite furnace atomic absorption spectrophotometry, Varian, Spectra AA 880Z) and total organic C (TOC – 5050 A, Shimadzu). An aliquot of the suspension was microwave - assisted digested using concentrated  $\text{HNO}_3$  as described in the EPA method 3015 and subsequently analyzed for As and Sb (ICPMS, Varian).

The turbidity of soil suspensions was determined using a turbidimeter (Hach 2100P ISO). In order to check the size of the particles in the supernatant the averaged volume-based size distribution of the colloids was analysed by dynamic light scattering (DLS, Malvern Instruments). The Zeta potential was calculated based on the electrophoretic mobility of the colloids, which was analysed by a Zetasizer 2000 photon correlation spectrometer (Malvern Instruments).

### ***5.3.5 Estimation of the fraction of organic- and mineral-dominated colloids – theoretical background***

Both separation methods are not able to strictly fractionate colloids according to their size. Other colloid properties control their assignment to different fractions. These controlling properties differ depending on the fractionation method: The separation of colloids in the filtration process is controlled by the size of the colloids as well as by the shape of the colloids, which may enable colloids larger than the specified pore size to penetrate the membrane anyway (and hence resulting in the passage of colloids which are larger than the actual pore size). With centrifugation it is not only the size but even more so the density of the individual colloids.

On one hand, these different fractionation principles of the applied techniques may limit the comparability of results. On the other hand the combined analysis of different results may help to quantify different groups of colloids as outlined in the following: Colloids can be classified into two different categories: a) colloids whose composition is dominated by organic material and b) colloids whose composition is dominated by mineral material such as Fe-, Al-, Mn-oxides and clay minerals. Provided that the filter permeability is equal for both colloid groups, MTUF is able to separate colloids into size classes, irrespective of the composition of the colloids. In contrast, centrifugation is only able to completely separate colloids according to their size, which are of similar density (equal or greater than the averaged density, which is  $2.65 \text{ g cm}^3$  in our case). In our centrifugation experiment, colloids dominated by mineral material will be fractionated correctly, while colloids dominated by organic material may be assigned to a smaller size fraction or even to the dissolved fraction. The degree of fractionation of organo-mineral colloids by centrifugation and hence the assignment to one of the groups depends greatly on the averaged density of the entire colloid, i. e. an organo-mineral colloid which is dominated by organic matter has a lower density than a colloid which is mainly composed of minerals. Based on these facts the combination of the results obtained from both methods can provide an estimate for the fraction of an element associated to i) colloids dominated by mineral material (centrifugation) and to ii) colloids dominated by organic material according to equations (5.1) and (5.2):

Percentage of element associated to **mineral-dominated colloids** = % of colloid-bound element as determined by centrifugation (5.1)

Percentage of element associated to **organo-dominated colloids** = (% of colloid-bound element as determined by MTUF) – (% of colloid-bound element as determined by centrifugation) (5.2)

Equation 5.1 and 5.2 can be applied to each individual size fraction. The estimate inherits some degree of uncertainty due to the unknown composition of organo-mineral colloids to which the individual element is associated with and may therefore only provide a ballpark figure. Positive results of equation (5.2) indicate the percentage of the individual element associated with organo-dominated colloids, negative results hint for the occurrence of the “filter effect”, i. e. centrifugation result exceed MTUF results. This is the case when larger colloids pass through the filter membrane. Since the percentage caused by this artefact proved very low it may be neglected in the calculation.

The overall percentage of an element bound to organo-dominated colloids across all size fractions can be calculated using equation (5.3):

$$\text{Total}_{(\text{Organo-dominated colloids})} = (100 \% - \text{MTUF}(<100 \text{ kDa})) - (100 \% - \text{Centrifugation}(< 100 \text{ kDa})).$$

### **5.3.6 Further characterization of the colloids**

In addition, energy dispersive X-ray (EDX; SAMx, software “IDFix”) analysis of the colloids was used to gain an understanding of the composition of the colloids in the < 1.2 µm filtrate. For the SEM/EDX analyses, the suspensions were applied to a glass carrier and were not coated prior to analysis.

## 5.4 Results and Discussion

### 5.4.1 Multi-stage tangential ultrafiltration

#### 5.4.1.1 Instrumental

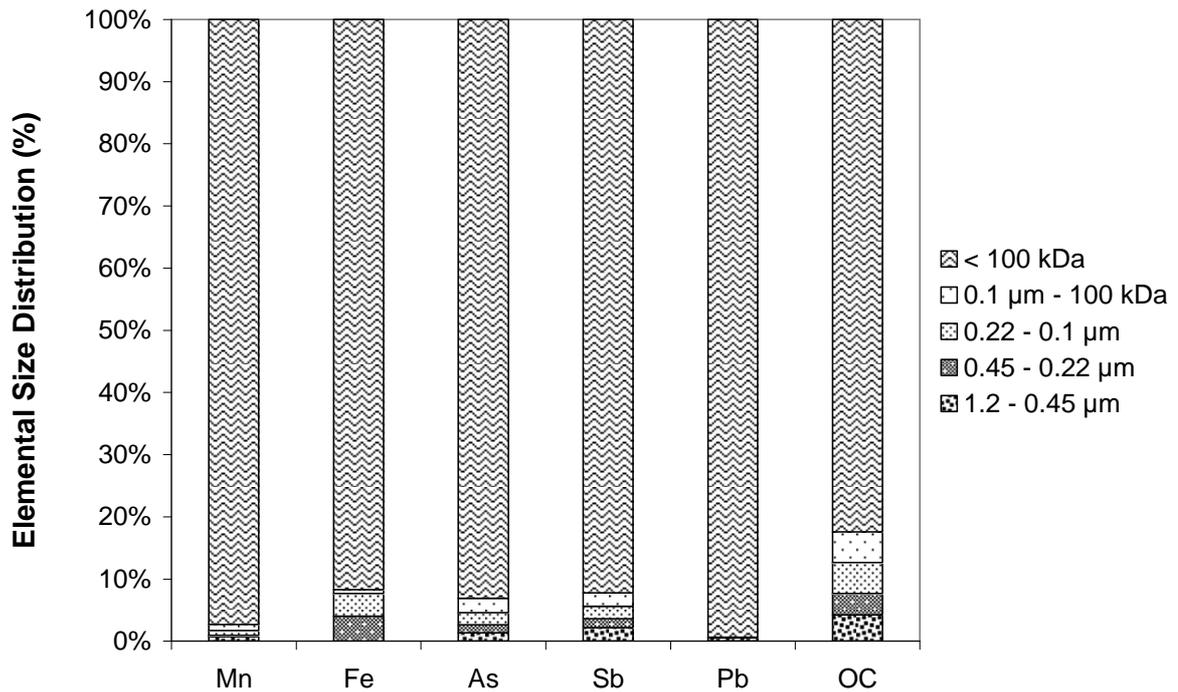
The averaged recovery rates for the individual elements (table 5.2) following separation showed some loss for the metals. Iron recoveries were lower than that found for other elements and variable between samples. The reproducibility of the element distribution across the different size fractions amounted to 85 – 100%. The analysis of digested filters proved that 10 to 18% of the overall Pb content (KOH treatment) and 25 to 30% of the overall Pb content (Ca(OH)<sub>2</sub> treatment) were attached to the membranes. This residual Pb was found mainly to be associated with the larger membranes (0.22 and 0.45 µm). The organic C recovery rate was slightly larger than 100%.

**Table 5.2:** MTUF recovery rates for the individual elements, averaged over the entire experiment (VC: variation coefficient)

	<b>Fe</b>	<b>Mn</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>C<sub>org</sub></b>
<b>Average recovery rate</b>	68 %	87 %	85 %	94 %	85 %	118 %
<b>VC</b>	29 %	8 %	8 %	5 %	8 %	7 %

#### 5.4.1.2 Colloid size and element distribution as determined by MTUF

Results of the control sample (pH of suspension: 4.7) clearly showed that hardly any metals were associated with colloids (table 5.3 and figure 5.1). The dissolved phase (< 100 kDa) dominated for all elements. Approx. 20% of organic C was present in colloidal form, being distributed in similar amounts over the different size fractions. A small percentage of Fe (9 %) was found in the colloidal fractions and may be due to its association with organic matter, possibly as Fe-DOM precipitates, which occur according to Jansen et al. (2005) at a pH of 4.5.



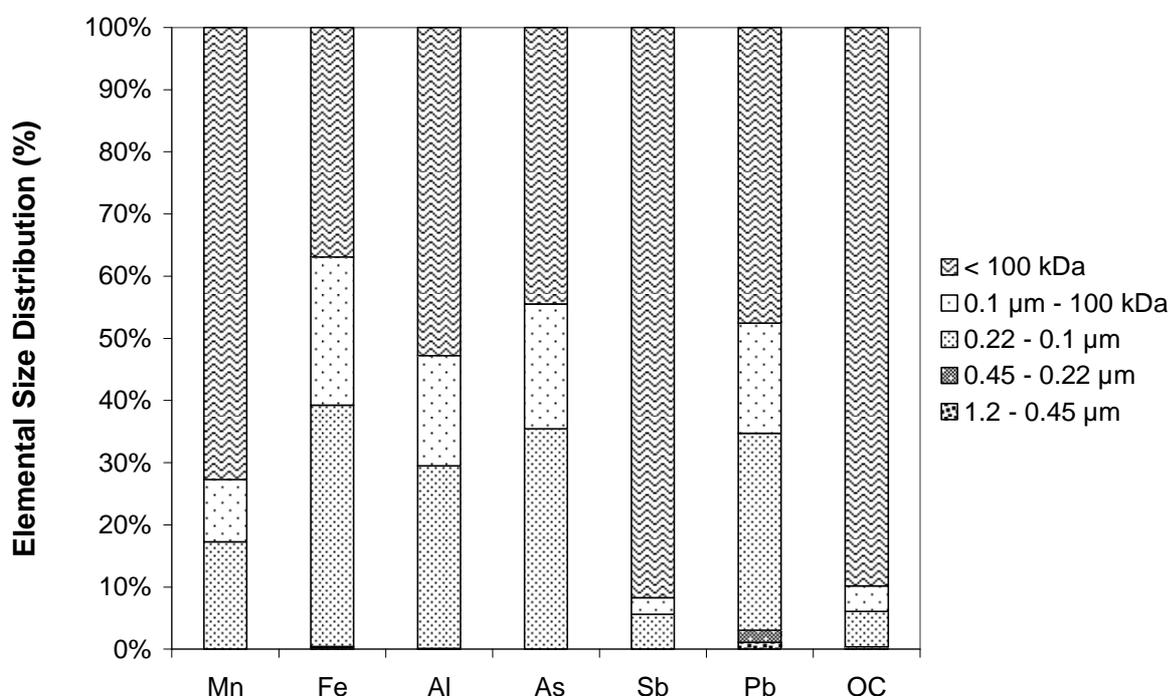
**Figure 5.1:** Elemental size distribution of the control sample (pH 4.7) following colloid separation by MTUF (OC: organic carbon)

**Table 5.3:** Dissolved and colloidal concentrations of the individual elements in the different treatments as obtained by MTUF (diss.: dissolved, coll: colloidal)

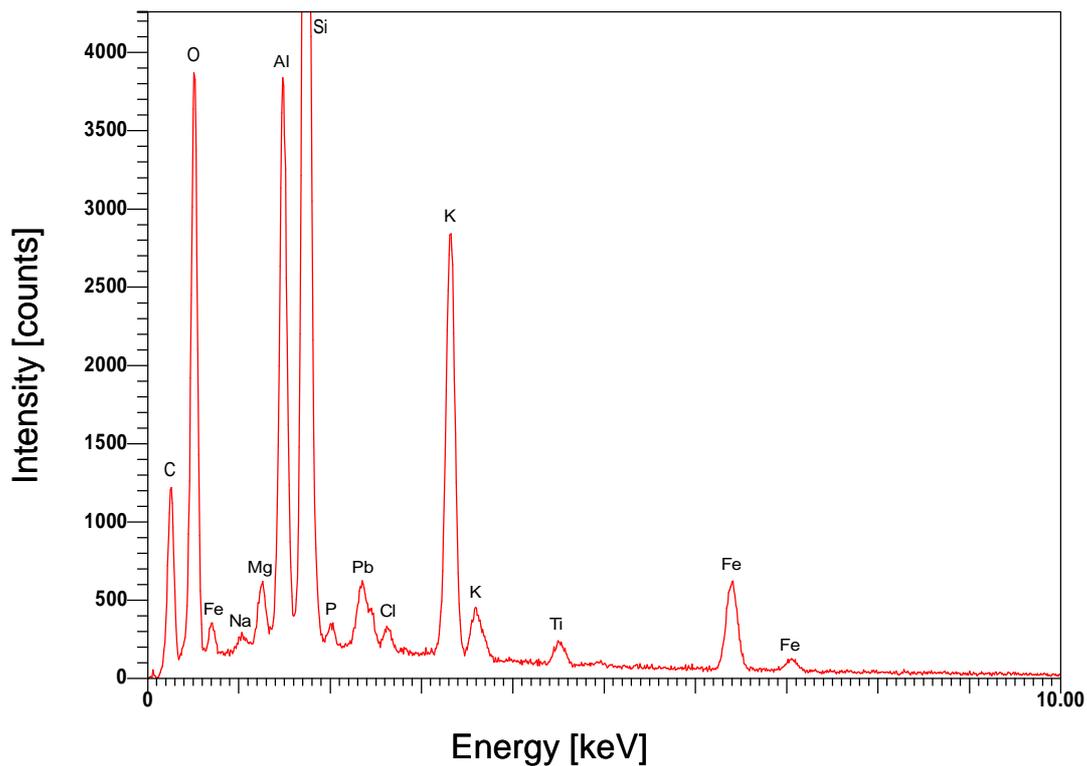
	Mn [ $\mu\text{g l}^{-1}$ ]		Fe [ $\mu\text{g l}^{-1}$ ]		Sb [ $\mu\text{g l}^{-1}$ ]		Pb [ $\mu\text{g l}^{-1}$ ]		As [ $\mu\text{g l}^{-1}$ ]		C <sub>org</sub> [ $\mu\text{g l}^{-1}$ ]	
	Diss.	Coll.	Diss.	Coll.								
Control	714	19	126	11	130	11	2675	17	27	2	71	15
KOH a	94	43	1777	4234	267	33	6844	7550	17	22	453	51
KOH b	94	35	2004	3422	184	17	6365	10690	20	26	187	42
Ca(OH) <sub>2</sub> a	52	1	246	9	142	2	924	642	9	0	53	1
Ca(OH) <sub>2</sub> b	65	4	299	58	186	5	1312	670	11	1	47	4

An increase in the soil suspension pH to 6.5 using KOH resulted in a complete change in both concentrations and elemental distribution (table 5.3 and figure 5.2). The concentration of most of the analytes increased in comparison to the control

sample. The large observed increase in dissolved Pb concentrations may be due to the strong increase in DOC concentration leading to a complexation of Pb (Turpeinen et al., 2000). Arsenic was found to be re-distributed between the dissolved and colloidal phase: in comparison to the control treatment (figure 5.1) dissolved concentrations decreased and colloidal concentrations increased, the latter probably due to the dispersion of sesquioxides. Interestingly, dissolved concentrations of As did not increase with increasing pH as commonly reported in the literature (for instance Tyler and Olsson, 2001). This may be due to the increased dispersion of sesquioxides, providing more sorption sites for As. The colloidal size fractionation pattern found for Pb and As is similar to that observed for the sesquioxide-forming elements (Fe and Al), which are predominantly found in the smaller colloidal size fractions (100 kDa – 220 nm). The identification of Al, Fe, Pb and oxygen in EDX-spectra suggests Pb to be associated with colloidal sesquioxides and clay minerals (figure 5.3). These observations are consistent with previous findings by Kabata-Pendias and Pendias (2001) who report the main sorbents of As to be Fe- and Al-oxides.



**Figure 5.2:** Elemental size distribution of the KOH treatment ( $\text{pH } 6.5 \pm 0.1$ ) following colloid separation by MTUF (OC: organic carbon)



**Figure 5.3:** EDX spectra of the KOH treatment

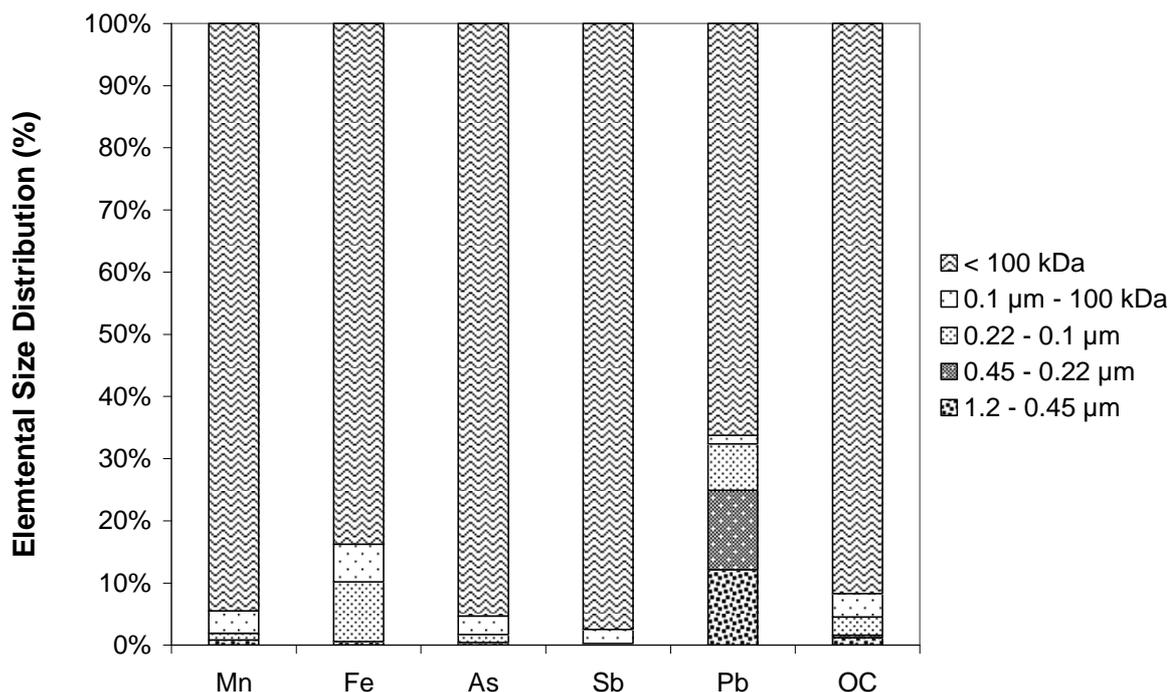
In spite of high concentrations, DOM did not displace As from the mineral colloid surfaces. This displacement might be expected according to results published by Redman et al. (2002) who found indications for the sorption competition between natural organic matter (NOM) and As.

Similar to the control treatment, organic C was mainly present in the dissolved fraction of the KOH treatment. However, the concentration of colloidal C is still larger in the KOH treatment than in the control treatment (table 5.3). We speculate, from results reported in the literature (e.g. Tipping and Higgins, 1982; Kretzschmar et al., 1997) that in part organic C is associated with inorganic colloids in the form of coatings enhancing colloid stability.

Although the state-of-the-art describes Sb to have similar adsorption-desorption properties as As (for instance Lintschinger et al., 1998) we did not find any parallels between these two elements in our experiment. With increasing dispersion of sesquioxides we only detected a small percentage of Sb in the colloidal fractions.

Contrarily to the findings of Johnson et al. (2005) who reported Sb to be completely sorbed at  $\text{pH} < 7$ , we still observed significant dissolved Sb concentrations following a pH increase to 6.5. In contrast to results published by Flynn et al. (2003), who observed only a minor influence of pH on the mobilisation of total Sb in soil water, concentrations of both dissolved and colloidal Sb were found to increase following a pH increase using KOH. A possible explanation for Sb to be present in the dissolved fraction is its association with DOM as previously described by Lintschinger et al., (1998). This assumption is supported by results of Mergenthaler and Richner (2002), who found a substantial fraction of Sb (17 to 44 %) bound to organic matter.

When the pH of the soil suspension was increased to 6.5 using  $\text{Ca}(\text{OH})_2$ , the distribution between dissolved and colloidal fractions changed strongly in comparison to both the KOH treatment and the control (figure 5.4).  $\text{Ca}(\text{OH})_2$  addition resulted in significantly lower dissolved concentrations of the individual elements than KOH addition (table 5.3). Arsenic, Fe, Pb, and DOM may have been retained by the soil matrix and/or were associated with particles larger than the filter cut-off (1.2  $\mu\text{m}$ ). This assumption may be attributed to the formation of “bridging” products between Ca and dissolved (Dahlgreen and Marett, 1991) or particulate organic matter, which are also thought to contain As and Fe (for example Fe-DOC-Ca-As). Similarly, from results reported by Celi et al. (2001), who found ortho-phosphate sorption on goethite to be increased in the presence of  $\text{Ca}^{2+}$ , we conclude enhanced As sorption due to bridging reactions on Fe-oxides. These oxides were retained by the soil matrix and contribute thus to a decrease in dissolved As concentration in the soil suspension. Besides, the formation of Ca-arsenate cannot be excluded. Our results are in contrast to those obtained by Jones et al. (1997) who reported increasing As concentrations following liming. The authors concluded As concentrations to correlate positively with pH, however, not with precipitation-dissolution reactions. Iron may have precipitated as metal hydroxide (Jansen et al., 2002). Due to the low concentrations of protons and DOM, Pb is not displaced from exchange sites. As a consequence of the described reactions, concentrations of dissolved As, Fe, Pb and DOM in the suspensions decreased.

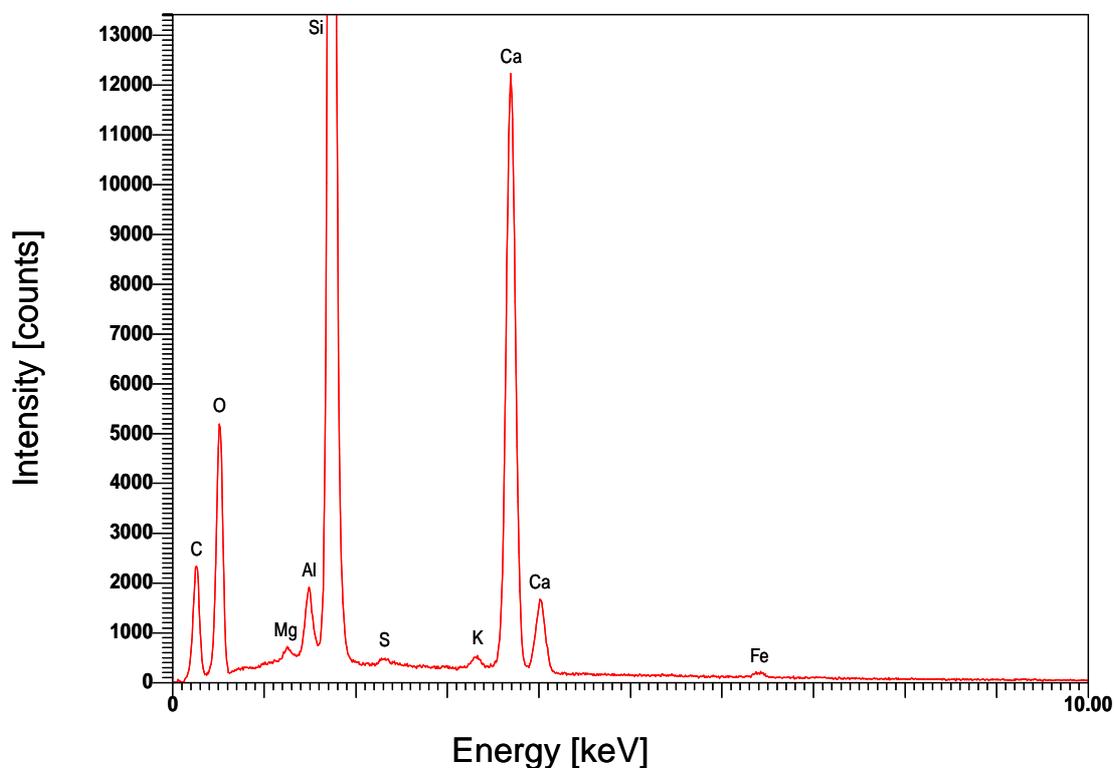


**Figure 5.4:** Elemental size distribution of the  $\text{Ca}(\text{OH})_2$  treatment ( $\text{pH } 6.5 \pm 0.1$ ) following colloid separation by MTUF (OC: organic carbon)

The EDX-spectra of the  $\text{Ca}(\text{OH})_2$  treatment (figure 5.5) identified C, O, and Ca as the main elements of the dispersed colloids and supports our assumption of the formation of “bridging” products between Ca and DOM. The absence of Pb from the colloidal fraction may be explained by two facts: (a) the competition between Ca and Pb for binding sites may lead to a displacement of Pb from the colloid (Harter, 1979) (b) the concentrations of Pb were below quantification limit. Therefore, the identification of Pb-bearing colloids remains an assumption which could finally not be confirmed by EDX measurements. As and Sb were below quantification limit in this treatment.

Elemental concentrations of the colloidal fractions may have decreased in comparison to the KOH treatment due to the suppression of colloid mobilization by the presence of the divalent  $\text{Ca}^{2+}$  cation as outlined by Kretzschmar et al. (1999). We observed a shift in the distribution pattern of colloid-associated Pb from smaller fractions (100 kDa – 220 nm as in the KOH treatment) to larger fractions (220 – 450 nm). Since Pb concentrations in solutions are below the solubility product of  $\text{Pb}(\text{OH})_2$  the presence of larger colloidal size fractions may be due to the formation of

“bridging” products between Ca-DOC-Pb as pointed out by Dahlgreen and Marett (1991).



**Figure 5.5:** EDX spectra of the  $\text{Ca}(\text{OH})_2$  treatment

## 5.4.2 Centrifugation

### 5.4.2.1 Colloid size and element distribution as determined by centrifugation

In general, the distribution of colloid-associated elements among the different size fractions as determined by centrifugation shows similar trends as the filtration-based distribution. However, the size of colloids determined by laser scattering strongly differs from the calculated size. Reasons for this apparent discrepancy and for differences between centrifugation and filtration results are discussed in the section below.

### 5.4.2.2 Turbidity and zeta potential

The turbidity of the individual supernatants continuously decreased with decreasing cut-off (results not shown) and is in agreement with the assumption of colloidal

particles being removed during the filtration process. In parallel, the zeta potential of colloids was found to become more positive with decreasing particle size (table 5.4). This suggests colloidal particles with negative charges were being removed from suspensions with decreasing particle size cut-off. The zeta potential of colloids in the  $\text{Ca(OH)}_2$  treatment was more positive than that of the KOH treatment. This observation may be explained by the formation of complexes between Ca and anionic groups of NOM (natural organic matter) “neutralising” some of the negative charge resulting in enhanced particle aggregation (Tiller and O’Melia, 1993).

**Table 5.4:** Zeta potential, Fe and DOC concentration of the supernatants of the different treatments (centrifugation)

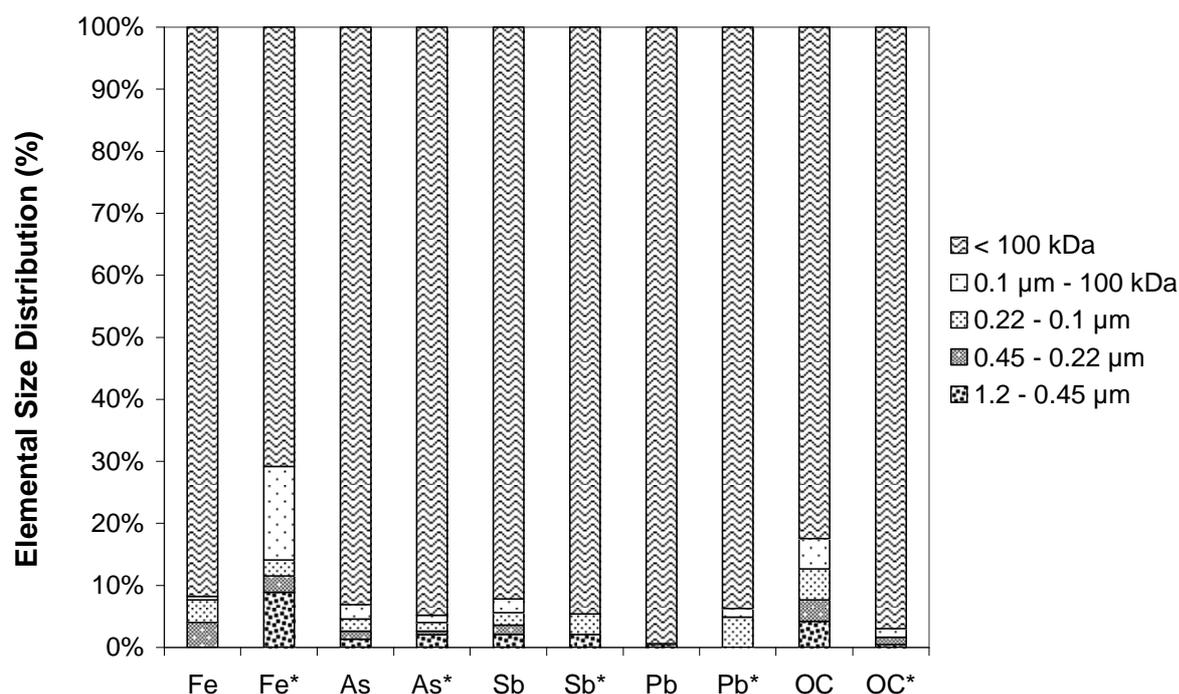
	Control	KOH			$\text{Ca(OH)}_2$		
	Zeta potential [mV]	Zeta potential [mV]	Fe [ $\mu\text{g l}^{-1}$ ]	DOC [ $\text{mg l}^{-1}$ ]	Zeta potential [mV]	Fe [ $\mu\text{g l}^{-1}$ ]	DOC [ $\text{mg l}^{-1}$ ]
Gesamt (<1.2 $\mu\text{m}$ )	-13.8	-21.4	3700	131.6	-14.3	788	85.3
< 0.45 $\mu\text{m}$	-14.0	-22.9	3650	126.9	-13.9	751	82.6
< 0.22 $\mu\text{m}$	-13.6	-22.1	3550	127.0	-14.2	723	82.5
< 0.1 $\mu\text{m}$	-11.4	-23.4	3450	128.2	-14.4	665	82.3
< 100 kDa	-11.1	-14.8	2450	123.9	-8.5	557	82.1

### **5.4.3 Colloid characterization by comparison and combination of results obtained by centrifugation and MTUF**

#### *5.4.3.1 Estimation of the fraction of organic- and mineral-dominated colloids*

In most cases, centrifugation showed a similar colloidal distribution pattern as MTUF. In general our results indicate that the distortion of the results is more affected by varying densities of the colloids rather than by the shape of colloids allowing for the penetration of particles larger than the actual pore size. The density effect gets most obvious for organic colloids. Calculating the centrifugation time required for colloids of a certain size to settle requires the assumption of an average density of  $2.65 \text{ g cm}^{-3}$ . However, the density of organic colloids may be much below that average ( $1.1 \text{ g cm}^{-3}$  (Citeau et al., 2001),  $< 1.6 \text{ g cm}^{-3}$  (Bethwell 2004)). Thus, we might have underestimated the fraction of COC by using centrifugation as a separation

technique as can be illustrated in the control treatment (figure 5.6) where centrifugation revealed a much lower percentage of COC than MTUF. This assumption is in agreement with findings by Wu et al. (2003) who found particles larger than the cut-off, which was calculated based on Stoke's law assuming an effective colloid density of  $2.65 \text{ g cm}^{-3}$ . They attribute this observation to the presence of organo-clay complexes with a density  $< 2.65 \text{ g cm}^{-3}$ .



**Figure 5.6:** Comparison of the elemental size distribution of the control treatment between results gained from MTUF and centrifugation (\*; OC: organic carbon)

Results of the KOH and the  $\text{Ca}(\text{OH})_2$  treatment obtained by equation (5.2) and (5.3), which differ significantly from zero (t-test with  $p < 0.1$ ) are displayed in table 5.5.

Deviations between the sum of each individual size fraction and the total amount of organo-dominated colloids (as obtained by equation 5.3) are ascribed to the fact that organo-dominated colloids still occur in size fractions for which the t-test does not show any significant difference between the data obtained by centrifugation and MTUF.

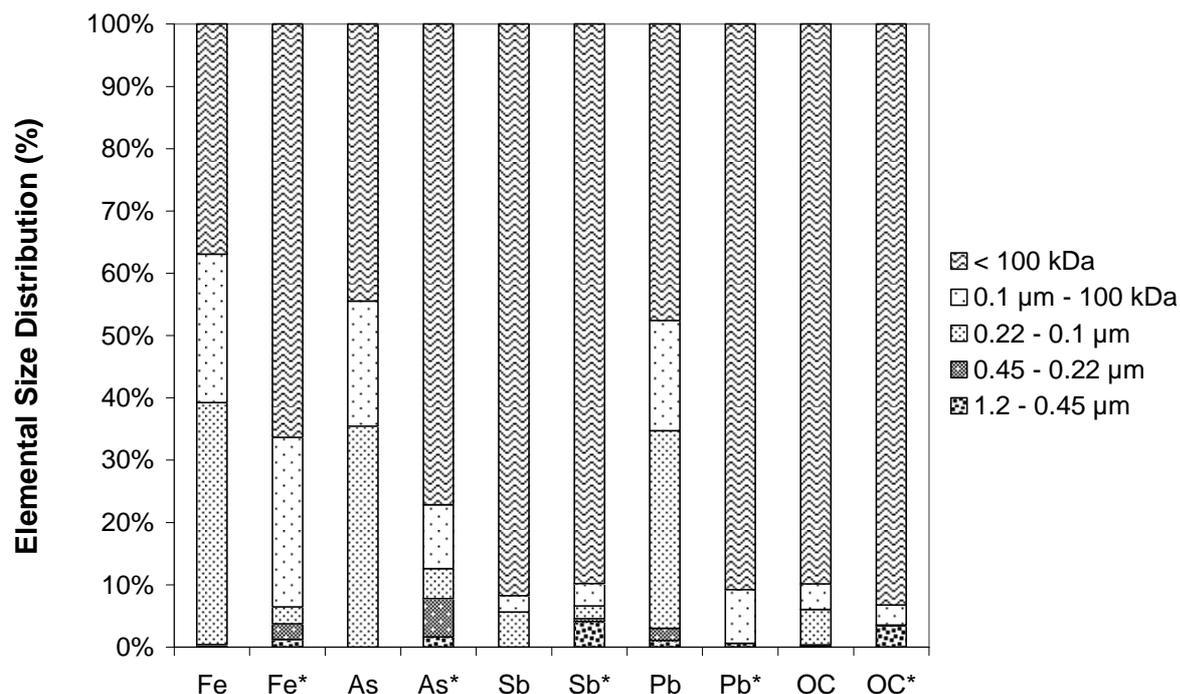
In the KOH treatment, Pb and Fe were only found in the smallest colloidal fraction (100 kDa – 100 nm) with sesquioxides most likely being coated by organic C (figure 5.7). This assumption is confirmed by the sharp change in zeta potential between

**Table 5.5:** Percentage of the individual element associated with mineral-dominated and organo-dominated colloids in the respective size fractions of MTUF and centrifugation as obtained by duplicate samples of the KOH- and Ca(OH)<sub>2</sub> treatment. The difference between MTUF and centrifugation in the individual size fractions (equation 5.2) and the total sum of colloids of all size fractions (equation 5.3) are listed for data points with  $p < 0.1$ .

Element	Size range	Percentage of the individual element associated with colloids in the respective size fraction [%] (MTUF)	Percentage of the individual element associated with <b>mineral-dominated colloids</b> [%] (Centrifugation )	Percentage of the individual element associated with <b>organo-dominated colloids</b> [%]
<b>KOH</b>				
Pb	0.22 – 0.1 $\mu\text{m}$	34	0	34
Pb	0.1 $\mu\text{m}$ – 100 kDa	17	9	8
Pb	Total (equ. 5.3)			48
Fe	0.22 – 0.1 $\mu\text{m}$	41	3	38
Fe	Total (equ. 5.3)			33
As	0.22 – 0.1 $\mu\text{m}$	36	5	31
As	Total (equ. 5.3)			33
<b>Ca(OH)<sub>2</sub></b>				
Pb	0.45 - 0.22 $\mu\text{m}$	14	2	12
Pb	0.22 – 0.1 $\mu\text{m}$	2	4	-2
Pb	Total (equ. 5.3)			25
Fe	1.2 – 0.45 $\mu\text{m}$	1	5	-4

the 100 kDa and 0.1  $\mu\text{m}$  supernatants, suggesting the separation of particles of negative charge. In the fraction of 100 – 220 nm centrifugation results differ from those obtained by MTUF: no colloidal Pb, Fe and organic C could be detected. We presume individual ions of Pb and Fe in the 220 – 100 nm fraction to be associated with organic matter (OM), which is not separated due to its lower density and therefore simulates the absence of colloid-associated Pb and Fe. This assumption is supported by the estimate provided by equation 3 (table 5.5). Similarly to Fe and Pb, As was found in the smaller colloidal size fraction (100 kDa – 100 nm), where it may be associated with sesquioxides (Kabata-Pendia, 2001). In the larger size fraction (100 – 220 nm) As was only detected to a small degree. This observation substantiates the assumption of As being associated with OM, either by “bridging” of

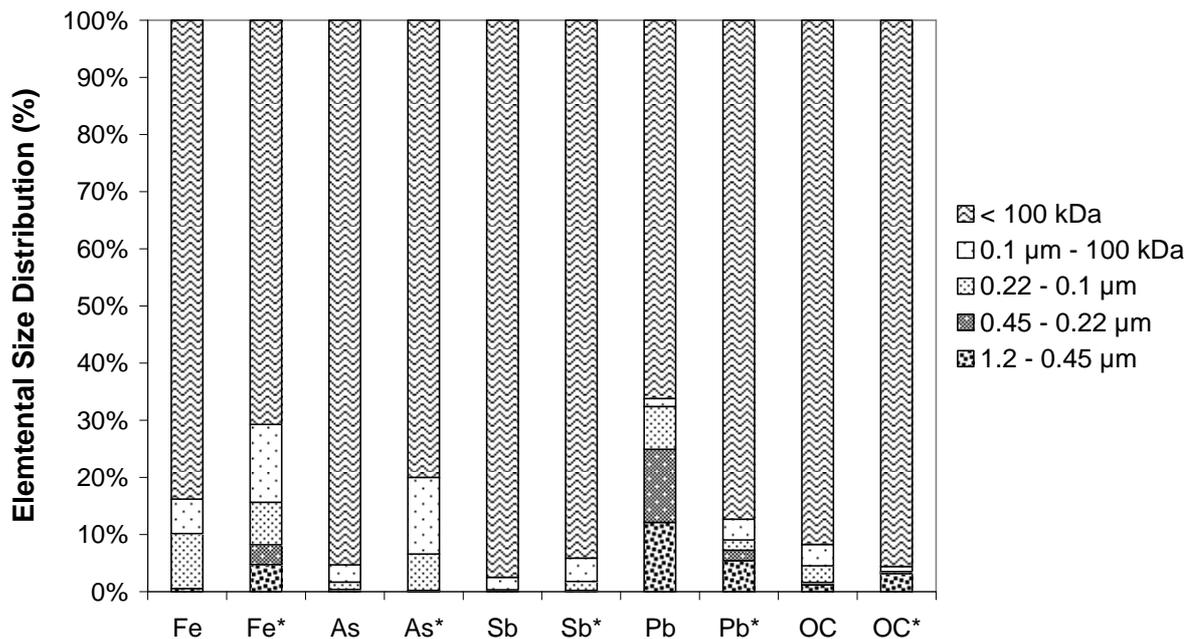
Fe between As and OM or directly with OM as described by Saada et al. (2003), who found As to be associated with amine groups of DOM. Since OM of this size fraction cannot be separated by means of centrifugation it is thought not to occur as coatings of sesquioxides, but as a “free” colloid. The assumption of As being associated with organic colloids is supported by results obtained by equation 5.3 (table 5.5).



**Figure 5.7:** Comparison of the elemental size distribution of the KOH treatment between results gained from MTUF and centrifugation (\*; OC: organic carbon)

In the  $\text{Ca}(\text{OH})_2$  treatment the centrifugation results for Fe and As differ from those found using the MTUF system (figure 5.8). The lower percentage of these elements in the colloidal fractions of the MTUF results, which was also observed for Fe in the control treatment, may be attributed to an artefact associated with the filtration process. For Fe in the  $\text{Ca}(\text{OH})_2$  treatment, this assumption could be confirmed by the result obtained by equation 5.3 (table 5.5). The pore size of the filter membranes is based on the assumption of spherical particles. However, colloidal material is often non-spherical. Therefore, longish particles of a rod- or needle-like shape such as these of Fe oxides would pass the membrane of smaller pore sizes anyway and thus decrease the concentration in the size fraction to which they would actually belong to and increase the concentration in the fraction below. In the  $\text{Ca}(\text{OH})_2$  treatment, the

colloid distribution of As follows the pattern found for Fe. In contrast to results obtained with MTUF, colloid-associated Pb was only detected to a minor degree. This observation supports the previously mentioned assumption of Pb being associated with DOM in the form of Ca-DOC-Pb-complexes. Due to its low density this compound is thought not be separable by means of centrifugation. The presence of an organo-Pb-colloid is substantiated by the result of equation 5.3 (table 5.5).



**Figure 5.8:** Comparison of the elemental size distribution of the  $\text{Ca}(\text{OH})_2$  treatment between results gained from MTUF and centrifugation (\*; OC: organic carbon)

#### 5.4.3.2 Particle size measurements by dynamic light scattering (DLS)

Particle size measurements were used in order to confirm the cut-offs calculated for the centrifugation experiment and to check the presence of any particles larger than the cut-off, which may occur due to a density lower than the one assumed in the calculation. The measurement technique was found to be subject to strong fluctuations especially as cut-offs were getting smaller and thus fewer particles were dispersed in suspension. With increasing centrifugation time (i. e. decreasing cut-off), the particle radius decreases (results not shown) in both treatments ( $\text{Ca}(\text{OH})_2$  and KOH). However, with decreasing cut-off, larger particles become increasingly

relevant again. Dynamic light scattering measurements did not show any larger particles in the Ca(OH)<sub>2</sub>-treatment as indicated by MTUF and as suggested in the literature (Celi et al., 2001).

Iron concentrations of all treatments decreased with decreasing particle size, whereas organic C concentrations hardly decreased (table 5.4). This observation was consistent with the assumption of inorganic particles (for instance oxides) getting separated during centrifugation (i. e. the number of large inorganic particles decreased). Meanwhile, the number of larger particles of smaller density (such as organics and clays) could remain constant and thus contribute to an increased averaged particle radius. Similar observations are reported by Wu et al. (2003) who attribute this phenomenon to the average hydrodynamic diameter of polydisperse samples to be biased towards the larger particles. Besides, they attribute this discrepancy to the non-spherical shape of particles.

The increasing presence of particles of larger size with calculated decreasing cut-off may also be explained by the low density of organic matter (table 5.6): the lower the density the larger the particle which remains in solution. In addition, it has to be mentioned that with decreasing particle size and with decreasing optical density of the sample the impact of contaminating dust particles may be increasingly relevant.

**Table 5.6:** Cut-off for different densities based on the same centrifugation parameters

Averaged density: <b>2.65 g cm<sup>-3</sup></b>	Density of organics: <b>1.5 g cm<sup>-3</sup></b>	Density of organics <b>1.2 g cm<sup>-3</sup></b>
Cut-off [nm]	Cut-off [nm]	Cut-off [nm]
450	818	1293
220	400	632
100	182	287
9	16	26

## 5.5 Conclusion

The combination of results gained from both MTUF and centrifugation allows for an estimate of the percentage of mineral-dominated and organo-dominated colloids. Moreover, the combination of both results allows for the conclusion whether colloidal organic C is associated with oxides or available as “free” colloidal organic C. However, each method inherits its own shortcomings and restrictions. In the filtration process, the spherical pore size of the filtration membranes allows larger particles of different shape (for instance rod- or needle-like) to pass the filter anyway and may thus distort the concentration pattern. On the other hand, centrifugation eliminates problems caused by membranes (such as build-up and adsorption). However, the assumption of an averaged particle density inevitably brings about an unclear cut-off. The major shortcoming of the centrifugation technique in studies dealing with colloids is the inability to completely separate colloidal organic C and associated elements from the suspension. Since colloidal organic C is thought to play a major role in environmental chemistry of colloids and associated contaminants we suggest the use of MTUF over centrifugation for colloid fractionation studies if a combined approach of both methods is not feasible.

Our study showed that the valency of the counterion controls quantity, elemental composition and size of the colloids. Increasing the pH using KOH led to the dispersion of sesquioxides and organic colloids. Colloidal Pb was found to be associated with sesquioxides which may be stabilized by organic C. This treatment also induced the mobilization of smaller colloids (100 kDa – 220 nm).

Increasing the pH using  $\text{Ca}(\text{OH})_2$  suppressed the dispersion of sesquioxides and induced the formation of larger colloids such as precipitation products of Pb and “bridging”-products of Ca and DOM, which may also include some Pb (for instance DOC-Ca-DOC-Pb). However, the precise composition of Pb-containing colloids in the  $\text{Ca}(\text{OH})_2$  treatment could finally not be confirmed by EDX measurements.

An understanding of colloid size and composition is essential in understanding the fate and behaviour of associated contaminants in terrestrial environments in order to

determine the risk to human and environmental health from the mobilization, stabilization and transport of colloidal fractions in potential stabilization procedures. Further research needs to be undertaken to characterize colloidal fractions in soils and determine the potential lability of associated elements in environments.

## 6 Mobilization of soluble and dispersible Pb, As, and Sb in a polluted, organic-rich Soil – Effects of pH Increase and Counterion Valency

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### 6.1 Abstract

Liming is a common technique suggested for the stabilization of shooting range sites. We investigated the effect of a pH increase on the mobilization of soluble and dispersible (colloidal) Pb, As, and Sb. Our hypothesis was that the addition of divalent cations counteracts the pH-induced mobilisation of soluble and colloidal metal(loid)s. We determined soluble and dispersible As, Pb, Sb, Fe and C<sub>org</sub> concentrations in the filtered (1.2 µm) suspensions of batch extracts of topsoil samples (C<sub>org</sub>: 8 %) from a former shooting range site following a pH increase to values between 3.5 and 7 by adding a monovalent (KOH) or a divalent (Ca(OH)<sub>2</sub>) base. In the Ca(OH)<sub>2</sub>-treated samples, soluble metal(loid) concentrations were 62 % to 98 % lower than in those treated with KOH. Similarly, Ca reduced dispersible Pb by 95 %, but had little or no impact on dispersible As and Sb. Our results show that Ca attenuates the mobilisation of both soluble and dispersible Pb and As in the soil. We conclude that the counterion valency controls the mobility of metal(loid)s by affecting the mobility and sorption capacity of the sorbents (e.g. colloids, organic matter).

## 6.2 Introduction

The contamination of shooting ranges by Pb, As and Sb may pose a significant environmental concern (USEPA, 2005). Amongst these three metals, Pb is of principle concern due to the high content in bullets (95 %; Neite et al., 1999) which often leads to severe contamination of the soil. The management of shooting ranges suggests liming for the remediation of such sites in order to reduce Pb migration (USEPA, 2005). Lime application impacts on the soil chemistry in two ways: (a) it leads to an increase of the soil pH and (b) and increases Ca concentration in the soil solution. With increasing pH, Pb concentrations in the soil solution decrease (Lindsay, 1979) due to enhanced retention by soil minerals (McBride, 1994). However, at higher pH, an enhanced release of soil organic matter promotes the formation of soluble organo-Pb complexes (Sauvé et al., 1998). In addition, the displacement of Pb from exchange sites by the addition of Ca ions (Harter, 1979) may contribute to increased dissolved Pb concentrations after lime application. While the impact of liming on dissolved Pb is well documented (for instance Turpeinen et al., 2000), detailed studies on the response of dissolved As and Sb to lime application are scarce if not absent. Whereas Pb in soils predominantly occurs as heavy metal cation, the metalloids As and Sb exist as negatively charged oxyanions. This explains relevant differences in sorption and retention of the metals.

Arsenic retention in soil is controlled by two types of sorbents, namely sesquioxides and organic matter. Sesquioxides are widely recognized as the main sorbents for As (for instance Kabata-Pendias and Pendias, 2001). Dissolved As concentrations in soil are reported to increase with increasing pH due to desorption from sesquioxides (Hsia et al., 1994; Smith et al., 1998). Recent studies also attribute an important role to soil organic matter in As retention (Warwick et al., 2005; Buschmann et al., 2006) with humic acids being found to play a major role in As retention in soil when the Fe-oxide content is low (Warwick et al., 2005). Suggested binding mechanisms for As with soil organic matter are the formation of inner- and outer-sphere complexes with phenolic and carboxylic groups (Mukhopadhyay and Sanyal, 2004) and H-bridges (Buschmann et al., 2006). Mobilization of dissolved organic C (DOC) induced by pH increase might therefore also mobilize associated As.

In addition to (de)sorption reactions, precipitation is a further mechanism which controls As solubility. Adding  $\text{Ca}^{2+}$  cations into the soil could also facilitate the formation of Ca-As-precipitates (Sadiq, 1997), resulting in a decrease in dissolved As. Similarly, Swash and Monhemius (1995) reported that the addition of lime reduced dissolved As concentrations.

Fe (hydr)oxides (Spuller et al., 2007), Al oxides (Tighe et al., 2005, Lintschinger et al., 1998, Brannon et al., 1985) and humic acid (Tighe et al., 2005) are reported to be - as with As - important sorbents for Sb in soil. Sb was found to be strongly sorbed to amorphous Fe-oxide at pH 3 to 6.5 (Tighe et al., 2005) and to hematite at pH < 7 (Edwards et al., 1999). In contrast to these mineral sorbents, the sorption of Sb to humic acids strongly decreases with increasing pH (Tighe et al., 2005). The authors attribute an important role to humic acid retention of Sb in soils with high organic matter content. Based on these findings, one may presume an increase in dissolved Sb concentrations following a pH increase if organic matter is the main binding partner of Sb in the soil. Furthermore, the addition of Ca may lead to the formation of  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ , which is suggested to control Sb(V) mobility at high concentrations (Johnson et al., 2005).

In order to assess the effect of liming on the mobilisation of pollutants colloidal forms have to be considered in addition to dissolved ones. Several studies emphasize the role of colloids for heavy metal transport in soils (Jensen et al., 1999, Egli et al., 1999; Denaix et al., 2001). A pH increase enhances the release and stability of colloids (Kretzschmar et al., 1999) liming may induce the mobilization of colloid-associated heavy metals. However,  $\text{Ca}^{2+}$  has a destabilizing effect on colloids leading to a compression or even collapse of the diffusive double layer (McBride, 1994) which facilitates particle aggregation. In addition, Kretzschmar and Sticher (1997) observed that the stabilizing effect of organic coatings was reduced by increasing  $\text{Ca}^{2+}$  concentrations due to the bridging effect of the bivalent  $\text{Ca}^{2+}$ .

Numerous studies indicate colloid-associated Pb mobilization and translocation to be a relevant pathway for Pb movement in soils (Jensen et al., 1999). However, there are very few studies on the occurrence of colloidal As (Buschmann et al., 2006) and

Sb (Buddemeier and Hunt, 1988) and detailed information on mobilization mechanisms and binding of the metalloids onto the colloids are absent. Considering the high affinity of As to sesquioxides (Kabata-Pendias and Pendias, 2001) and complexation with dissolved organic matter (Buschmann et al., 2006) we assume colloidal As mobilization to be important in soils. The following processes and binding mechanisms may be relevant for the association of As and Sb with colloids: a) An increase in pH might produce new sorption sites, e. g. by the dispersion of As- and Sb-sorbing colloids. b) Complexation of As (Mukhopadhyay and Sanyal, 2004; Buschmann et al., 2006) and Sb (Tighe et al., 2005) with humic acids may enhance their sorption to colloidal organic matter. c) A pH increase might induce the formation of cation bridges in the presence of polyvalent cations (for instance bridging products between Ca, As and dissolved organic matter (DOM) as described by Redman et al., 2002).

Whilst the role of sesquioxides in the context of As and Sb retention in soils is well documented, there are only few studies investigating the role of organic matter. Furthermore, there are no studies focusing on colloid mobilization in organic-rich soils. Therefore, the aim of our work is to investigate the influence of a pH increase on the mobilization of soluble and dispersible Pb, As, and Sb in a soil with mainly organic sorbents. We tested the hypothesis that divalent cations attenuate the mobilising effect of increasing pH by a) “neutralizing” negative colloid charge and therefore contributing to enhanced colloid flocculation and by b) immobilizing dissolved As and Sb by the formation of inorganic precipitates such as  $\text{Ca}_3(\text{AsO}_4)_2$  and  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ .

## **6.3 Materials and Methods**

### ***6.3.1 Soil sampling and soil characterization***

We selected a soil with a comparatively high  $C_{\text{org}}$  and low sesquioxide concentration. Samples were taken from the top soil (Ah-horizon) of a former shooting range in North Rhine-Westphalia, Germany, wooded with 30-year-old oak trees. The soil's parent material is a fluvial, sandy stream deposit of the Pleistocene. The soil was

classified (according to World Reference Base) as Podzolic Cambisol with a texture of loamy sand.

We determined the pH in deionized water and 0.01 M CaCl<sub>2</sub> solution, using 10 g air-dried soil and 25 ml of the respective solution (pH Meter 761 Calimatic, Knick). The suspensions were left to stand for 1 hour before the pH was measured. Organic C and N (C<sub>org</sub> and N<sub>tot</sub>) were measured by a C and N-analyser (Carlo Erba Instruments, type C/N NA 1500 N) after drying the soil at 105 °C. For the determination of the water content, field-moist samples were dried at 105 °C until they reached constant weight. To measure total acid-soluble As, Al, Fe, Mn and Pb the soil was digested with concentrated HNO<sub>3</sub> in closed vessels (two replicates), following the procedure described by Ilg et al. (2004). The digested samples were filtered, transferred into volumetric flasks and filled to the mark with deionized water. This solution was analyzed as described in the analysis section. Total Sb of the soil was determined by X-ray fluorescence analysis (Philips PW2400 X-ray spectrometer DY 818) in the form of a powder tablet. Oxalate-extractable Fe and Al were determined by adding 100 mL of ammoniumoxalate/oxalic acid solution to 5 g of air-dried soil. The mixture was shaken for 2 hours and subsequently filtered over a folded filter. The obtained filtrates were analysed as described in the analysis section. The determined soil physico-chemical characteristics are presented in table 6.1.

**Table 6.1:** Soil properties

<b>Paramter</b>	<b>Value</b>
pH <sub>H<sub>2</sub>O</sub>	4.3
pH <sub>CaCl<sub>2</sub></sub>	3.7
C/N	36.05
C [g kg <sup>-1</sup> ]	80.0
N [g kg <sup>-1</sup> ]	2.2
Pb [mg kg <sup>-1</sup> ]	495
As [mg kg <sup>-1</sup> ]	4
Sb [mg kg <sup>-1</sup> ]	34
Al [mg kg <sup>-1</sup> ]	2534
Fe [mg kg <sup>-1</sup> ]	933
Mn [mg kg <sup>-1</sup> ]	27
Al <sub>ox</sub> [mg kg <sup>-1</sup> ]	700
Fe <sub>ox</sub> [mg kg <sup>-1</sup> ]	318

### **6.3.2 Dispersion experiments**

As there are currently no standard methods for the determination of the stability of soil colloids batch experiments are commonly used to determine the dispersibility of colloids. We studied the mobilization of colloidal and soluble Pb, As and Sb in batch experiments using field-moist samples (< 2 mm) and a soil to water ratio of 1:10. The samples were shaken for 16 hours on an end-over-end-shaker (10 rpm; GFL 3040).

For the comparison of a pH increase induced by a monovalent and a divalent base we set up the following series: K-treatment: We added appropriate quantities of 0.1 M KOH and 0.1 M KNO<sub>3</sub> solution to adjust the pH to 3.5, 4.3, 6.2 and 7.1. Ca-treatment: We added 0.005 M Ca(OH)<sub>2</sub> and 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub>·4 H<sub>2</sub>O solutions to adjust the pH to 3.7, 4.4, 5.3, and 6.1. To obtain pH 5.3 and 6.1 we also added solid Ca(OH)<sub>2</sub>. We adjusted the pH to 6.7 by adding 0.005 M Ca(OH)<sub>2</sub> solution and solid Ca(OH)<sub>2</sub>. The ionic strength of each individual batch of both treatments was kept constant by adding required amounts of KNO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> solution, respectively, amounting to 15 mM.

At the end of the experiment pH was checked in the suspensions prior to filtration through a 1.2-µm cellulose-nitrate-membrane (Sartorius, Type 11303 – 047N). An aliquot of the filtrate was acidified (pH < 1) with concentrated nitric acid for the measurement of the total Pb, As, Sb, and Fe concentration in solution. In addition, we determined concentrations of total organic C (TOC), turbidity, particle size and zeta potential (analytical methods see below). An aliquot of the filtrate was ultracentrifuged at 156 000 x g for 3 hours at 10 °C (Beckman Optima TL) in order to separate colloids larger than 10 nm and a density > 1.2 g cm<sup>3</sup> (based on Stoke's law) from the solution. The supernatant was transferred into plastic containers, acidified with nitric acid and analysed for concentrations of dissolved Pb, As, Sb, Fe and organic C (DOC). The difference of the metal and C concentration between non-ultracentrifuged and ultracentrifuged samples accounts for colloidal metal and C fractions (defined operationally).

### **6.3.3 Analyses**

Arsenic was measured by ICP-MS (Varian), Pb and Fe by graphite-furnance atomic absorption spectroscopy (Spectra AA 880Z, Varian) at a wavelength of 217.0 nm (Pb) and 248.3 nm (Fe), respectively. Oxalate-extractable Al and Fe concentrations were determined by flame atomic absorption spectroscopy (Perkin Elmer 1100 B) at wavelengths of 309.3 nm (Al) and 248.3 nm (Fe), The organic C concentration of the solutions was measured by a total organic carbon analyser (TOC – 5050 A, Shimadzu).

The turbidity of soil suspensions was determined using a turbidimeter (Hach 2100P ISO). In order to check the size of the particles in the supernatant the averaged volume-based size distribution of the colloids was analysed by dynamic light scattering (DLS, Malvern Instruments). The Zeta potential was calculated based on the electrophoretic mobility of the colloids, which was analysed by a Zetasizer 2000 photon correlation spectrometer (Malvern Instruments).

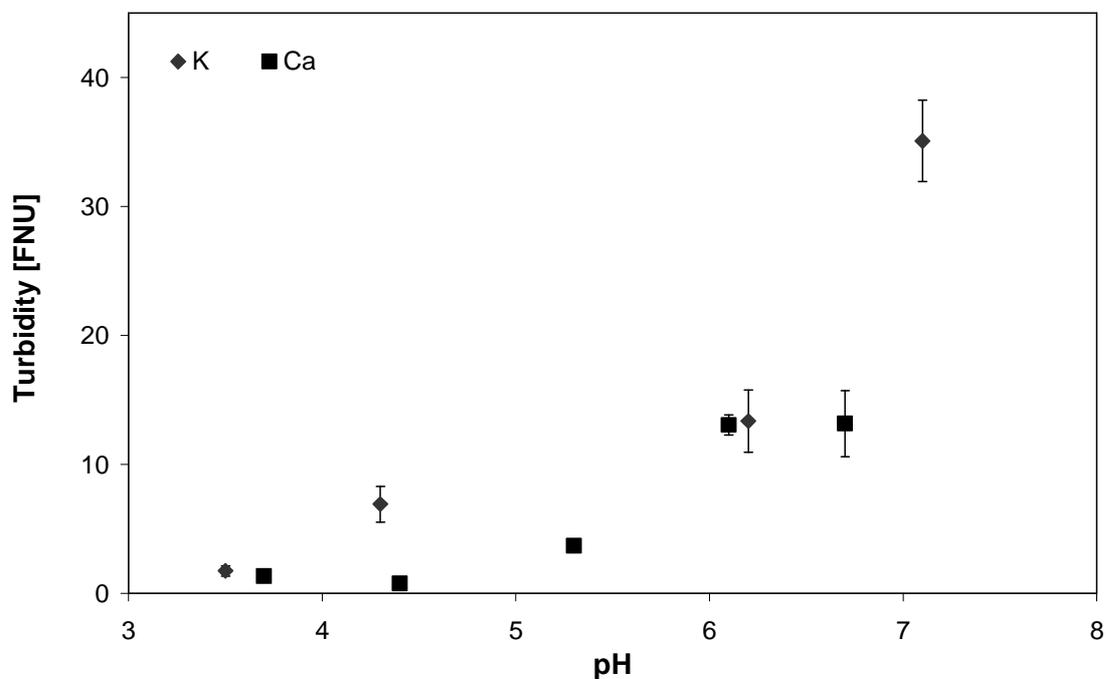
The error bars depicted in the figures represent the experimental error of triplicate samples.

## **6.4 Results and Discussion**

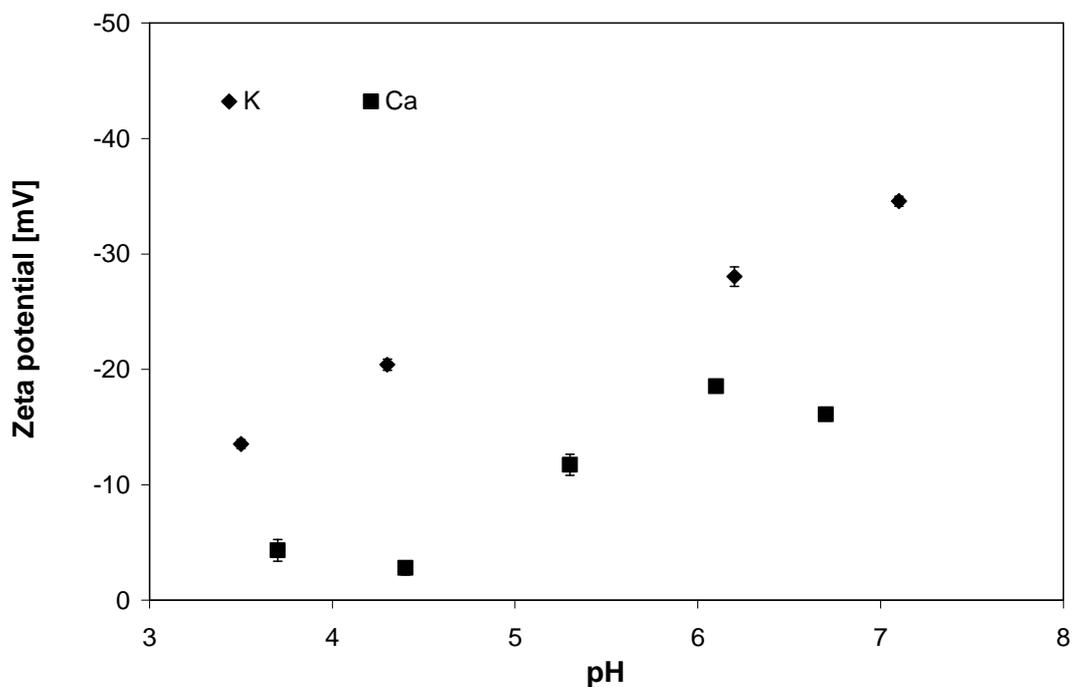
### **6.4.1 Colloid mobilization**

With increasing pH the amount of dispersed colloids increased in both treatments (figure 6.1). In the presence of the  $\text{Ca}^{2+}$  cation, however, this increase is offset to higher pH values. In addition, the amount of dispersed colloids is less than in the presence of the monovalent  $\text{K}^+$  cation. With increasing pH zeta potential values of the colloids become increasingly negative (figure 6.2). Again, this pH-induced charge effect is less pronounced in the Ca treatment than in the K treatment. While  $\text{K}^+$  adsorbs non-specifically, specific adsorption of  $\text{Ca}^{2+}$  to anionic groups of natural organic matter leads to the compensation of the negative colloid charge as explained by Tipping and Cooke (1982). Therefore,  $\text{Ca}^{2+}$  results partly in enhanced colloid

flocculation (Tiller and O’Melia, 1993) which is reflected in decreased turbidity values of the Ca treatment (figure 6.2). The particle size ranged from approximately 300 to 1000 nm. The pH and the valency of the counterion had no significant effect on colloid size (data not shown).



**Figure 6.1:** Turbidity as a function of pH for the KOH and Ca(OH)<sub>2</sub> treatment (bars depict one standard error)



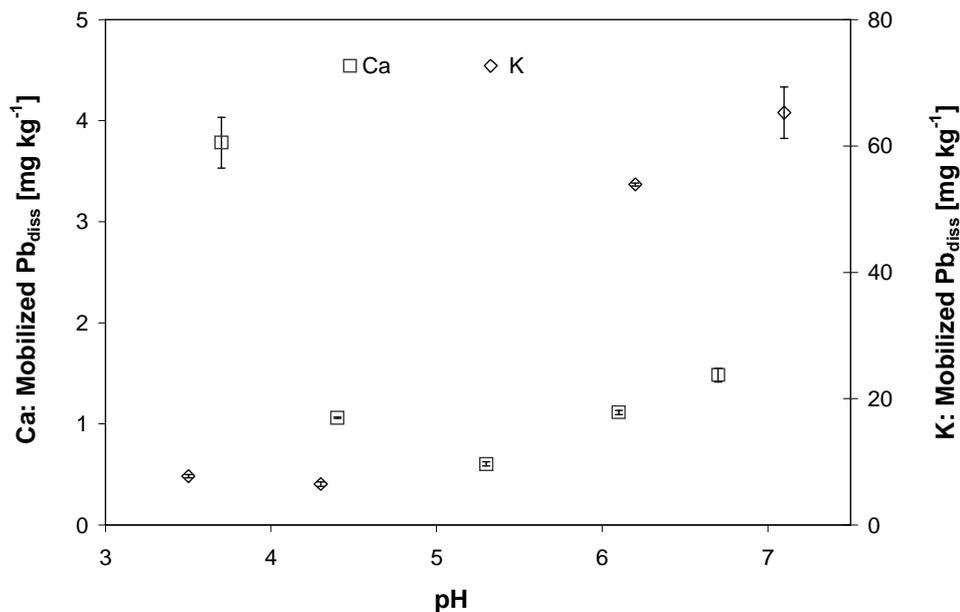
**Figure 6.2:** Zeta potential as a function of pH for the KOH and Ca(OH)<sub>2</sub> treatment (bars depict one standard error)

### 6.4.2 Mobilization of soluble and dispersible Pb, As, and Sb

The comparatively low concentration of sesquioxides and high concentration of organic C of our study soil suggests organic matter to be the dominant binding partner of Pb, As and Sb. An increase in pH results in the enhanced release of both soluble and dispersible organic C with this increase in the presence of the monovalent cation being much more pronounced than in the presence of the divalent cation (data not shown).

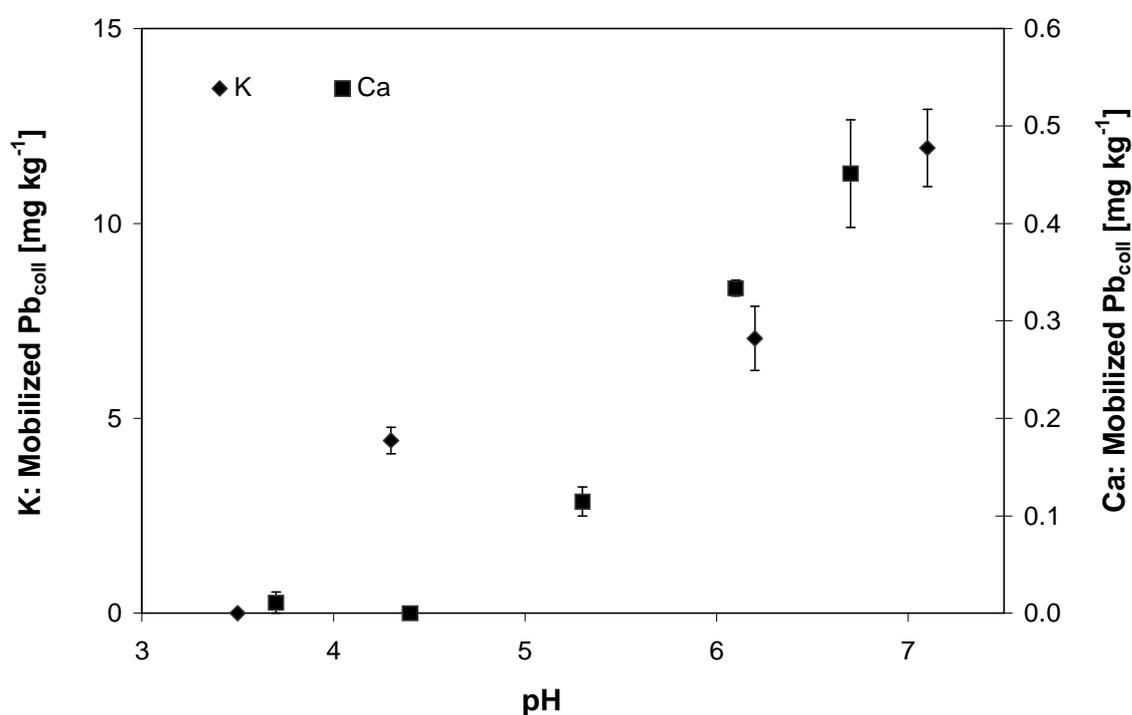
#### 6.4.2.1 Lead

The concentrations of both colloidal and dissolved Pb increase following the pH increase induced by addition of KOH (figure 6.3a and 6.3b). In the presence of the divalent Ca cation however, dissolved and colloidal concentrations differ from the KOH-treated samples. The decrease of dissolved Pb concentrations reached a minimum at pH 5.3 after which they rose with increasing pH. Since Ca decreased the pool of mobilized DOC available for Pb-complexation, at pH values near 5.3 Pb is to a great part removed from solution by either precipitation as  $\text{Pb}(\text{OH})_2$  or by adsorption onto the solid phase. At pH values greater than 5.3, however, the negative charges of deprotonated carboxyl groups exceed the amount of positive charges of the Ca cation. As a consequence, concentrations of DOM and thus also concentrations of dissolved organically bound Pb increase.



**Figure 6.3a:** Mobilized dissolved Pb as a function of pH for the KOH (K) and  $\text{Ca}(\text{OH})_2$  (Ca) treatment (bars depict one standard error)

Colloidal Pb in the  $\text{Ca}(\text{OH})_2$ -treated samples could only be detected at  $\text{pH} > 4.4$  where the increasingly negative particle charge induced by a pH increase is no longer compensated by Ca cations. However, Ca (in comparison to K) did not attenuate the concentration of colloids (i. e. the turbidity) to the same degree as concentrations of colloidal Pb. Therefore, Pb-displacement from the colloid by Ca due to competition for binding sites as described by Harter (1979) might additionally cause a decrease in colloidal Pb concentrations.

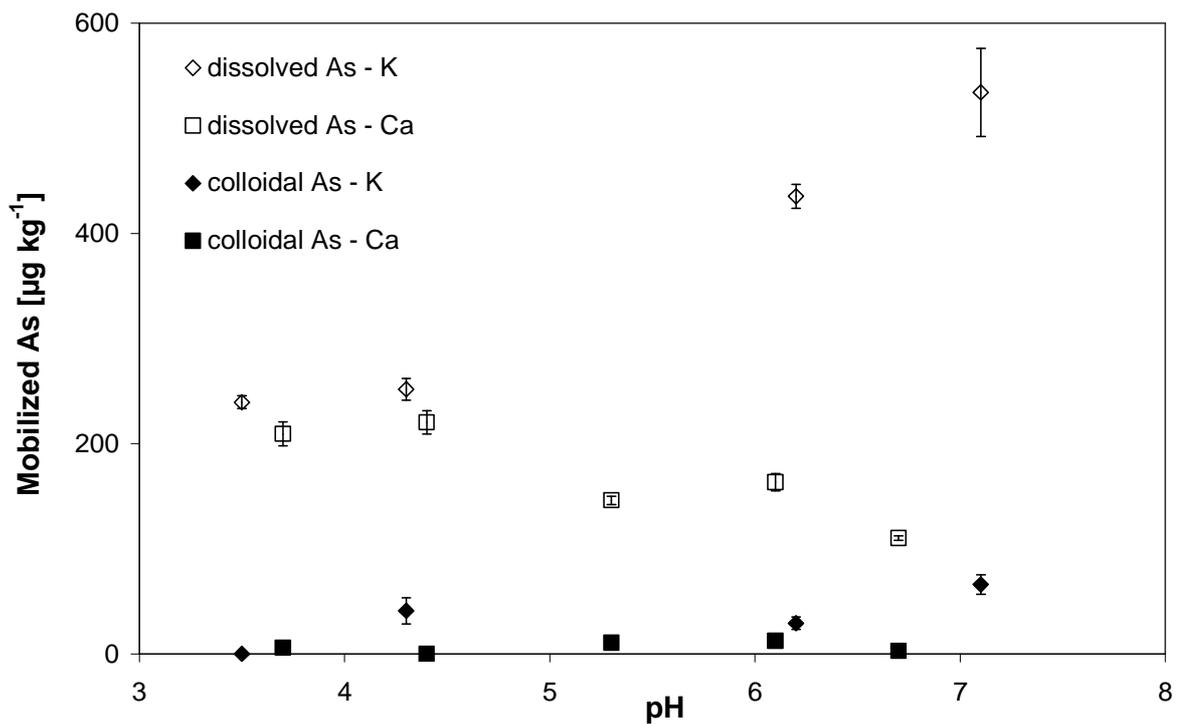


**Figure 6.3b:** Mobilized colloidal Pb as a function of pH for the KOH (K) and  $\text{Ca}(\text{OH})_2$  (Ca) treatment (bars depict one standard error)

#### 6.4.2.2 Arsenic

Dissolved As increases with increasing pH in the presence of the monovalent cation ( $R^2 = 0.94$ , figure 6.4) in accordance with results reported by Smith et al. (1998), suggesting As-desorption from sesquioxides. In addition, the pH-induced dissolution of humic acids to which (according to Warwick et al., 2006) As is adsorbed to, may explain the increase in dissolved As. Colloidal As concentrations (figure 6.4) in this treatment are much lower than dissolved concentrations suggesting As has only a minor association with colloids. Even though colloidal Fe and colloidal organic C concentrations increase continuously with increasing pH (data not shown), colloidal

As concentrations remain constant and do not show any pH-dependence. This implies limited availability of colloidal binding sites for As. The high ratio between organic C and Fe and organic C and Al suggests possible As-sorption sites provided by sesquioxides to be greatly reduced by the presence of organic coatings. Possible As-binding sites on organic matter, such as amino groups (Thanabalasingam and Pickering, 1986), are more abundant near the mineral surface where they are being adsorbed (as described in the model proposed by Kleber et al., 2007). This reduced availability caused by direct blockage of sorption sites provided by the mineral surface and by a reduction in the accessibility of these sites allows for a very limited As sorption. A further explanation for the occurrence of only little colloidal As is the presence of Fe-organic clusters. The accessibility of organic functional groups suitable for the binding of As in these clusters would be very low.



**Figure 6.4:** Mobilized dissolved (blank symbols) and colloidal (filled symbols) As as a function of pH for the KOH (K) and  $\text{Ca}(\text{OH})_2$ (Ca) treatment (bars depict one standard error)

The addition of the Ca cation led to a continuous decrease in dissolved As with increasing pH. These findings are in line with Voigt et al. (1996), who report the addition of  $\text{Ca}(\text{OH})_2$  to reduce exchangeable As. Since the formation of  $\text{Ca}_3(\text{AsO}_4)_2$  in our suspensions may be ruled out based on calculations of the solubility product,

the observed decline in dissolved As may be attributed to increased “bridging” with increasing pH as suggested by the mechanism described by Redman et al. (2002): negatively charged As anions and DOM are linked by positively charged Ca cations. Similarly, Thanabalasingam and Pickering (1986) found polyvalent cations enhance As sorption to humic acids providing evidence for our assumption that Ca crosslinks between several arsenate and DOM ions to form larger compounds. Since we did not detect any colloidal As in the  $\text{Ca}(\text{OH})_2$  treatment we assume the formed bridging products to be either retained by the soil matrix or to be dispersed in suspension in a size exceeding our filter cut-off (1.2  $\mu\text{m}$ ).

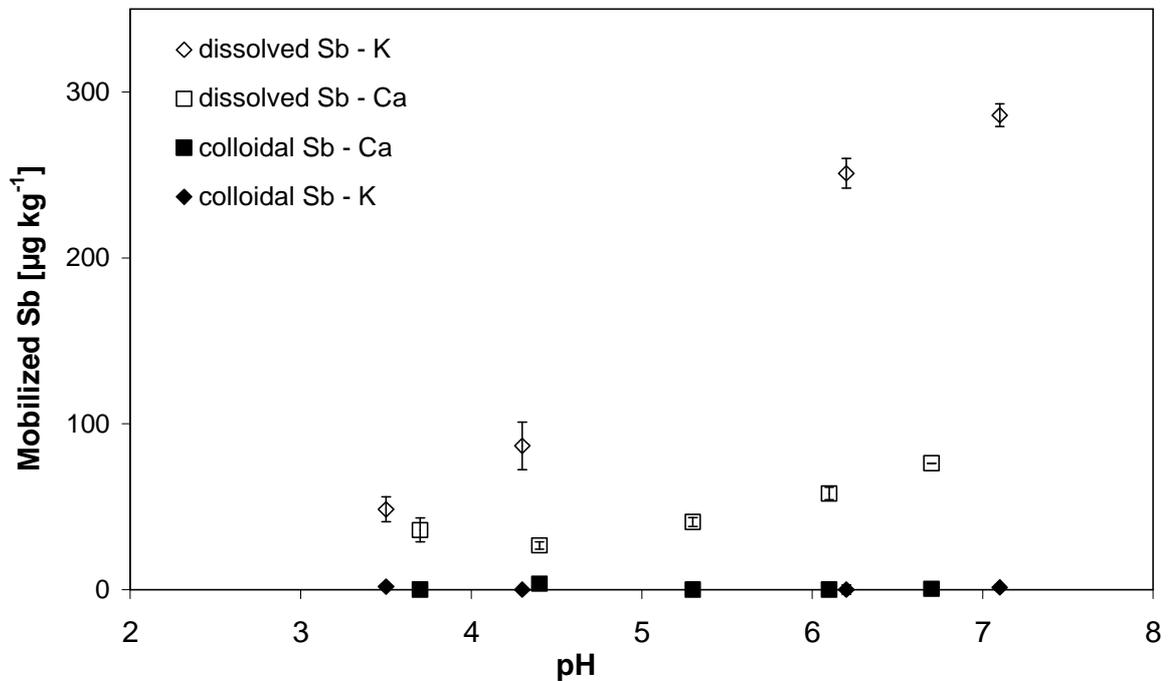
#### 6.4.2.3 Antimony

Similarly to As, organic matter is postulated to be the main binding partner of Sb in this soil due to the low concentrations of Fe and Al. Dissolved Sb concentrations increase following a pH increase in both treatments, with the increase being more pronounced after the addition of KOH (figure 6.5). The increase in dissolved Sb in the KOH treatment is in agreement with Tighe et al. (2005), who reported sorption of Sb(V) by humic acid decreasing as the pH increases. In the KOH treatment, dissolved Sb shows the same response to a pH increase as dissolved As.

While interactions between As, Ca and dissolved organic matter have already been reported (Redman et al., 2002) studies describing the role of cation bridging between organic matter and Sb are absent. In the presence of Ca cations, our results show an increase in dissolved Sb concentrations with increasing pH suggesting that Sb does not bridge to non-mobile or aggregated organic matter to the same extent as As. We ascribe this observation to the different accessibility of the negative charge of these two anions caused by differences in their chemical structure: In the arsenate anion, As forms covalent bonds with oxygen- and hydroxyl-groups in a tetrahedral structure with the negative charge being located at the deprotonated oxygen atom at the edge of the ion, where it is freely accessible by other ions in solution. In the case of  $\text{Ca}^{2+}$  this allows for bridging reactions between As and DOM leading to the flocculation of DOM-Ca-As-consisting compounds. In the  $\text{Sb}[(\text{OH})_6]^-$ -complex, however, the negative charge is located at the Sb atom which is coordinated by 6 octahedral OH-groups (King et al., 1995) with these OH-groups shielding the negative charge. The shielded negative charge of the Sb anion would render

bridging between increasingly negatively charged DOM and Sb by the Ca cation more difficult. The assumption that Sb does not bridge with Ca ions is supported by the fact that the ratio of Sb/DOC in both treatments (data not shown) does not differ significantly from each other. Since Sb may be associated with DOM (Tighe et al., 2005) and therefore co-dissolution with DOC may be possible, the equal Sb/DOC-ratio indicates that the lower mobilization of soluble Sb in the  $\text{Ca}(\text{OH})_2$  treatment is due to less DOM mobilization and not due to bridging of Ca.

Antimony was not found to be associated with colloids in any treatment (figure 6.5). The precipitation of Ca-antimony could be ruled out since dissolved concentrations of Sb were below the solubility product.



**Figure 6.5:** Mobilized dissolved (blank symbols) and colloidal (filled symbols) Sb as a function of pH for the KOH (K) and  $\text{Ca}(\text{OH})_2$ (Ca) treatment (bars depict one standard error)

## 6.5 Conclusion

Our experiments demonstrate that Ca counteracts the pH effect. Whereas the formation of  $\text{Ca}_3(\text{AsO}_4)_2$  precipitates may be ruled out Ca was found to impact on the mobilization of sorbents. The presented results suggest that the counterion valency controls the mobility and sorption capacity of the sorbents (i.e. colloids, DOM):

(a) It governs (i) the mobilization of colloids by impacting on colloid charge and (ii) the mobilization of DOM by flocculation.

(b) It governs the interactions of the metal(loid)s with the soil sorbents and therefore impacts on dissolved (i.e. Pb-DOC-complexation, formation of insoluble “bridging products” between As, Ca, and organic matter) and colloidal (competition for binding sites between Ca and Pb) metal(loid) concentrations.

Future research should address the role of the  $\text{Ca}^{2+}$  cation in the interactions between As/Sb, DOM and  $\text{Ca}^{2+}$  in defined systems.

Our data indicates that while liming-induced pH increase does not pose any major risk of colloidal As and Sb mobilization as long as divalent cations dominate in solution the mobilization of soluble Sb needs to be considered. Risk assessment of limed sites should not only address dissolved, but also colloidal Pb concentrations to avoid potential Pb leaching. Further studies are needed to address the role of varying sorbent composition in colloidal metal(loid) mobilization.

# 7 Synthesis and general Conclusions

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## 7.1 The governing role of soil solid phase composition in soluble and dispersible metal(loid) mobilization in the context of drying and liming

The overall data suggest that the composition of the soil solid phase, i. e.  $C_{org}$  and sesquioxide concentration, may turn the balance in favour or against the mobilization of the individual dissolved or colloidal metal(loid) phase. In the following sections, I will discuss this assertion in more detail and elucidate the role of the composition of the soil sorbents and dispersible colloids in the context of both soluble and dispersible metal(loid) mobilization.

### 7.1.1 Drying

My results of chapter 3 demonstrate that the effect of drying on colloid mobilization depends on the concentration of soil organic C: Whilst in “low  $C_{org}$ -soils” ( $C_{org}$  concentration between 2.0 and 5.6 %) drying led to either an immobilization of colloids or to no significant change in colloid mobilization, it led to a pronounced increase in the amount of mobilized colloids in a soil with a  $C_{org}$  concentration of 24.5 % (“high  $C_{org}$ -soil”). In the latter, organic colloids were mobilized while in the “low  $C_{org}$ -soils” mineral colloids were immobilized. In most cases of the “low  $C_{org}$ -soils” these changes went along with a decrease in mobilized colloidal heavy metal concentrations, whereas in the soil containing 24.5 %  $C_{org}$  no significant increase in colloidal heavy metal mobilization could be found. While drying-induced mobilization of DOC had no effect on dissolved concentrations of Cd, Pb, and Zn it caused a redistribution of Cu from the colloidal to the dissolved phase. These findings indicate that the concentration of organic matter plays a key role in both the (im)mobilization of colloids as well as the mobilization of soluble and colloidal heavy metals.

### 7.1.2 Liming

The soils used for the investigations of the effects of a pH increase and counterion valency (chapter 4 and 6) differ in their  $C_{org}$  concentration and  $C_{org}/Fe_{tot}$ -ratio (table 7.1).

**Table 7.1:**  $C_{org}$  concentration and  $C_{org}/Fe_{tot}$ -ratio of the soils used in chapter 4 and 6

	$C_{org}$ [g kg <sup>-1</sup> ]	$Fe_{tot}$ [g kg <sup>-1</sup> ]	Ratio $C_{org}/Fe_{tot}$ (based on moles)
Soil 1 (chapter 4)	209	3.1	221
Soil 2 (chapter 6)	80	0.9	314

The ratio between  $C_{org}$  concentration and added  $Ca(OH)_2$  (as required to adjust pH 7, data not shown) is similar in both soils. This indicates that organic matter makes up the major part of the base neutralization capacity and that the amounts of base neutralizing functional groups (i.e. carboxyl groups) per mass unit of organic matter are the same in both soils.

The soils show an onset in colloid mobilization at different pH values in the presence of the Ca ion (figure 7.1), which is in line with colloidal Pb mobilization: In the soil with a  $C_{org}$  concentration of 80 g kg<sup>-1</sup> I could detect a pronounced colloid mobilization at pH > 4.4. This increase in mobilized colloids following  $Ca(OH)_2$ -addition takes place at lower pH values than in the soil with a  $C_{org}$  concentration of 209 g kg<sup>-1</sup> where I observed a strong increase in mobilized colloids only at pH values > 5.8. The onset in colloid mobilization goes along with a very pronounced increase in the negative colloid charge (figure 7.2). At pH > 4.4, however, colloid charge of the soil with a concentration of 80 g kg<sup>-1</sup>  $C_{org}$  was much more negative than in the soil with a concentration of 209 g kg<sup>-1</sup>  $C_{org}$ , explaining the stronger dispersion of colloids. However, these results appear contradictory to findings by numerous authors who report the mobilization and stabilization of colloids to be enhanced by DOM since it increases the negative colloid charge (Kretzschmar, 1999; Kaplan et al., 1996; Heil and Sposito, 1993).

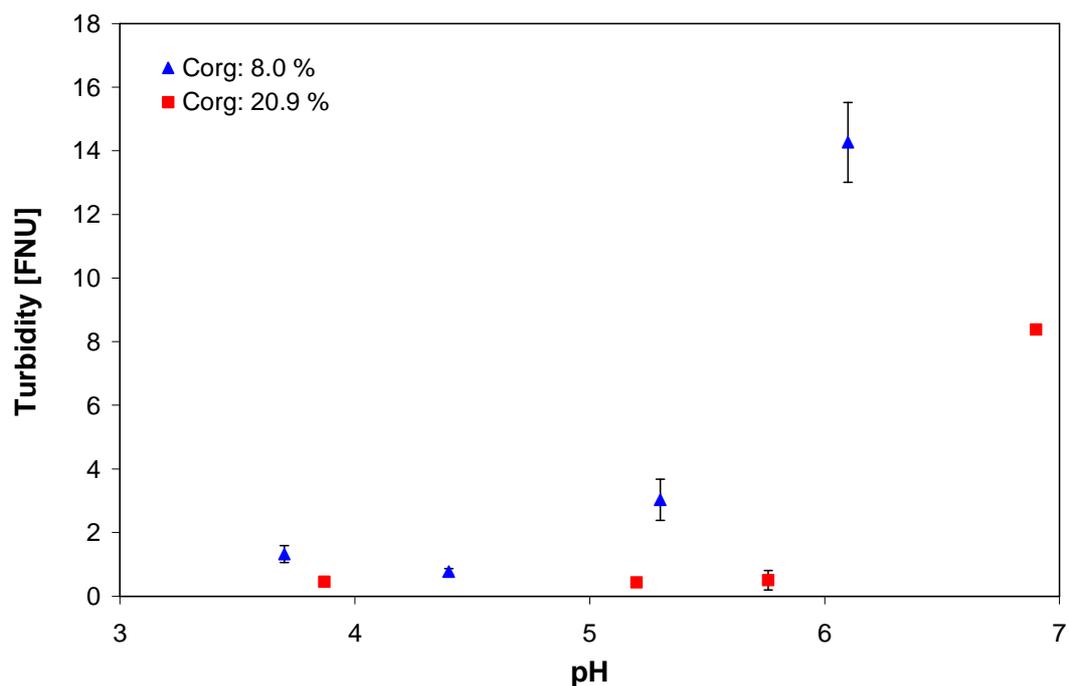
Since the base neutralization capacity, i.e. the amount of base neutralizing functional groups (i.e. carboxyl groups) per mass unit organic matter of the soils is similar this

parameter may be ruled out to explain the different pH at which colloid mobilization starts, but there are several possible explanations for this apparent contradiction.

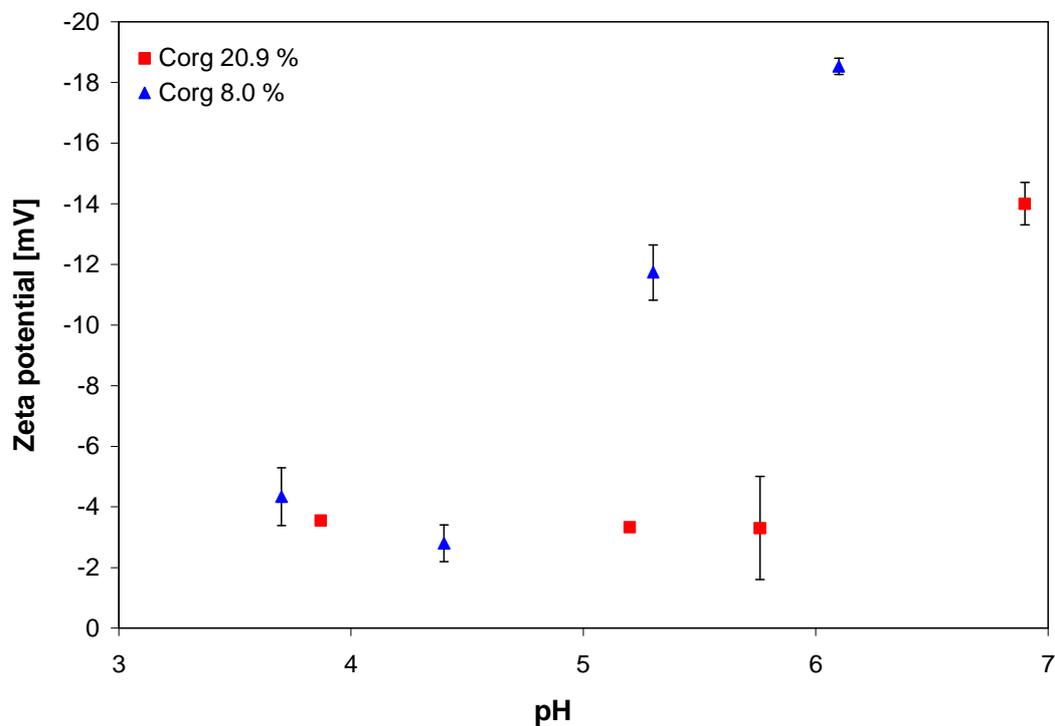
*Ionic strength.* The ionic strength of the soil with a concentration of  $209 \text{ g kg}^{-1} \text{ C}_{\text{org}}$  is approximately 3 times greater than the ionic strength of the soil with a concentration of  $80 \text{ g kg}^{-1} \text{ C}_{\text{org}}$ . Since for same electrolytes, an increasing ionic strength results in a decreasing zeta potential (Müller, 1996) this could explain the lower zeta potential of the soil with a  $\text{C}_{\text{org}}$  concentration of  $209 \text{ g kg}^{-1}$ .

*Different ratios between the  $\text{C}_{\text{org}}$  and  $\text{Fe}_{\text{tot}}$  concentrations of the soils.* The zeta potential of colloids is governed by the sum of negatively and positively charged sites (i. e. negatively charged functional groups of organic matter and positively charged surfaces of inorganic minerals such as Fe- or Al-(hydr)oxides). Different ratios between the  $\text{Fe}_{\text{tot}}$  and  $\text{C}_{\text{org}}$  concentrations could therefore explain why the soil with a concentration of  $80 \text{ g kg}^{-1} \text{ C}_{\text{org}}$  shows greater negative charges at  $\text{pH} > 4.4$  than the soil with a concentration of  $209 \text{ g kg}^{-1} \text{ C}_{\text{org}}$  (figure 7.2): The relative amount of dispersible Fe-(hydr)oxides in the soil with a  $\text{C}_{\text{org}}/\text{Fe}_{\text{tot}}$  ratio of 314 is lower than in the soil with a  $\text{C}_{\text{org}}/\text{Fe}_{\text{tot}}$  ratio of 221. This means that the relative contribution of positively charged Fe-(hydr)oxides to the averaged zeta potential is less, thus resulting in lower overall negative charges than in the soil with a  $\text{C}_{\text{org}}/\text{Fe}_{\text{tot}}$  ratio of 221.

In addition, the larger  $\text{Fe}_{\text{tot}}$  concentration of soil 1 may provide a further explanation. Supposing the colloidal Fe concentrations in the suspensions are greater in soil 1 than in soil 2, the lower zeta potential in soil 1 could be a result of additional crosslinking reactions between Fe and organic matter (Schaumann, 2006), resulting in a compensation of negatively charged functional groups.



**Figure 7.1:** Turbidity of soil suspensions of soil 1 and 2 with a high and a low concentration of organic matter as a function of pH ( $\text{Ca}(\text{OH})$  treatment; bars depict one standard error)



**Figure 7.2:** Zeta potential of soil 1 and soil 2 with a high and a low concentration of organic matter as a function of pH ( $\text{Ca}(\text{OH})_2$  treatment; bars depict one standard error)

These observations indicate that the composition of soil colloids may play an important role in colloid mobilization since it may control the onset pH of colloid mobilization.

The experiments discussed in chapter 5 and 6 were conducted on soils with similar  $C_{org}$  concentrations, but greatly different concentrations in oxalate-extractable Al and Fe. In the following, they are therefore referred to as high and low C/Fe-soil, respectively. These two types of soils provide differently composed (a) sorbents for dissolved metal(loid)s and (b) pools of potentially mobilizable colloids. My results show that in these two soils a pH increase in the presence of a monovalent and a divalent counterion leads to differences in the mobilization of both soluble and colloidal Pb, As and Sb. In addition, different types of colloids are mobilized providing various types of sorption sites for different metal(loid)s (Lyvén et al., 2003). The provision of dispersed sorption sites does not only affect colloidal metal concentrations but also dissolved ones. In the following, I will compare relevant differences and outline similarities in soluble and dispersible metal(loid) mobilization between the two types of soils and discuss responsible mechanisms.

### *7.1.2.1 Lead*

I did not detect any difference in the influence of the KOH treatment on the mobilization of colloidal and soluble Pb between the two types of soils. However, in the  $Ca(OH)_2$  treatment of the low C/Fe-soil, a pH increase from the soil original pH 5.0 to pH 6.5 resulted in decreasing dissolved Pb concentrations, whereas they increased in the high C/Fe-soil following the pH minimum at pH 5.3. This difference might be ascribed to the smaller ratio between dissolved Pb and DOC of the high C/Fe-soil, implying enough DOC to allow for Pb complexation. In the low C/Fe-soil, the higher concentrations of mobilized Fe diminished the DOC-pool available for Pb-complexation, resulting in a decrease in dissolved Pb concentrations. However, since in the low C/Fe-soil, there are only two data points, pH 4.7 and 6.5, it is impossible to define the minimum of the curve and therefore I cannot rule out increasing concentrations at higher pH.

### 7.1.2.2 Arsenic

The response of As to a pH increase in the presence of a monovalent base differed strongly between both soils. Whilst dissolved As concentrations in the high C/Fe-soil increased, presumably due to the dissolution of organic matter to which according to Warwick et al. (2005) As is associated with, concentrations dropped in the low C/Fe-soil. I ascribe this difference in As distribution to the presence of different sorption sites in both soils. In the low C/Fe-soil, micro-aggregate dispersion of sesquioxide-bearing colloids may provide a high amount of high-affinity sorption sites for As, leading to an increasing colloidal As and consequently decreasing dissolved As concentration. In that context it is interesting to note that even though the total concentration of colloidal As increased, the amount of As sorbed per g Fe-containing colloids decreased from pH 4.7 (17.9  $\mu\text{g As/g Fe}$ ) to pH 6.5 (5.2  $\mu\text{g As/g Fe}$ ). This indicates that with increasing pH, As desorbs from colloidal sesquioxides. However, due to the great release of As-sorbing colloids, net concentrations of colloidal As still increase.

A pH increase in the presence of a divalent cation led to decreasing concentrations in both dissolved and colloidal As.

### 7.1.2.3 Antimony

Results of the low C/Fe-soil show a similar response to increasing pH as the high C/Fe-soil: dissolved Sb concentrations increase following a pH-increase to 6.5, with the increase being more pronounced in the KOH than in the  $\text{Ca(OH)}_2$  treatment. The observed pH-dependence of the low C/Fe-soil is in conflict with findings reported by Tighe et al. (2005), who report > 99 % to be absorbed by amorphous  $\text{Fe(OH)}_3$  regardless of pH. This mechanism would suggest very low dissolved Sb concentrations. However, if sesquioxides or -hydroxides are partly coated with organic matter – which is, considering the elevated DOC concentrations, very likely the case in the low C/Fe-soil – organic matter would act as a main binding partner. As the pH increases and organic matter begins to dissolve, associated Sb would also dissolve. This mechanism could explain the increase in dissolved Sb with increasing pH. It therefore points out a governing role of organic matter in Sb mobilization. While there is no colloidal Sb in the high C/Fe-soil, there is some in the

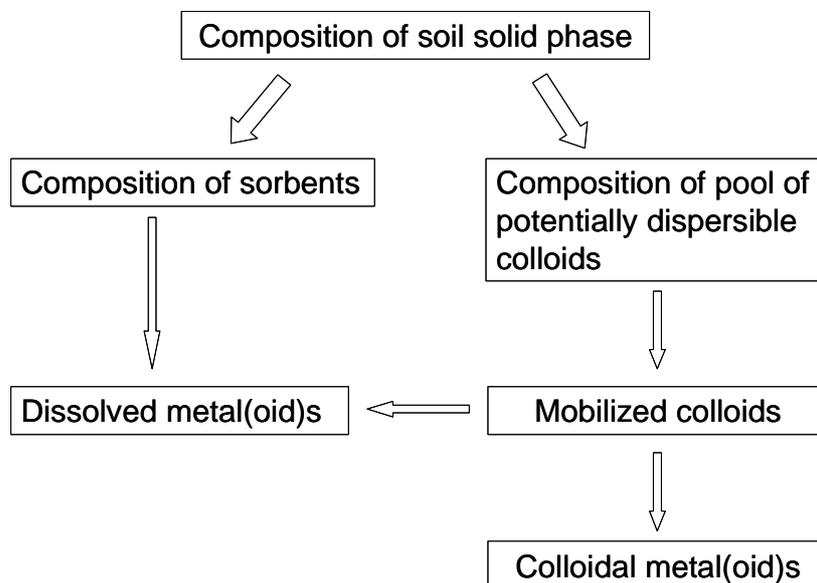
low C/Fe-soil. It increases slightly following the addition of KOH and drops after  $\text{Ca}(\text{OH})_2$ -addition, suggesting a possible association of Sb with colloidal sesquioxides, whose dispersion is enhanced in the presence of the monovalent cation and decreased in the presence of the divalent cation.

### ***7.1.3 Is there a critical zeta potential for colloid mobilization?***

The zeta potential as a measure for the colloid surface charge is a governing parameter for colloid stability (Séquaris and Lewandowski, 2003). Considering the zeta potential across all measured samples my data set suggests colloid mobilization to show a pronounced increase at a zeta potential  $< -14$  mV (figure 7.3). This is similar to results by Séquaris and Lewandowski (2003), who report colloid release in batch experiments with agricultural top soil ( $C_{\text{org}}$ : 2 to 5 %) to start at zeta potential values  $< -16$  mV. However, both values are less negative than the critical zeta potential reported in the study by Johnson (1999). At similar ionic strength, the author found zeta potentials on quartz sand of  $-34$  mV. This difference in critical zeta potential between colloids mobilized from top soil samples and quartz sand could be ascribed to steric effects as described by Heil and Sposito (1993), which come additionally into play on organic colloids or organic-coated mineral colloids. Considering the organic-rich matrices ( $C_{\text{org}}$  concentration  $\geq 8$  %) of all my soil samples I presume steric stabilization might be an effect in addition to the zeta potential, enhancing colloid stability as suggested by Kretzschmar et al. (1997).



showed different responses to environmental changes. While organic colloids were mobilized in a drying event, inorganic colloids were immobilized.



**Figure 7.4:** Relation between the soil solid phase, soil sorbents and colloidal and dissolved metal(oid)s

The data suggest that in the context of a liming-induced pH increase colloid composition may determine the onset-pH of colloid mobilisation. Furthermore, colloid composition governs whether a pH increase leads to an increase or decrease in the respective concentrations of dissolved or colloidal metal(oid)s. Dissolved and colloidal Pb may be increased following a liming-induced pH increase if a certain minimum pH is exceeded. This pH minimum is determined by the ratio between organic and inorganic colloidal components. Whilst the mobilization of colloidal As and Sb does not seem to be of any relevance in a liming-induced pH increase, I observed decreasing dissolved As concentrations, but increasing dissolved Sb concentrations. It became obvious that the three metals of main concern on shooting range sites may respond differently to a pH increase. According to the US CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) List As and Pb are ranked as the metals with the highest environmental concern since they are “determined to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure” at seriously contaminated sites (ATSDR, 2005). Since Pb makes out the highest percentage of

the overall contamination I suggest increasing the pH as far as to the pH minimum of soluble and colloidal Pb mobilization (i. e. in my studied acidic forest soil of chapter 6 to pH 4.4 and 5.3, respectively). This pH would also assure decreasing dissolved As concentrations and risks only a minor increase in dissolved Sb concentrations.

These results suggest that on sites, which are contaminated by metal(loid)s differing in their responses to lime application, a differentiated approach is necessary. The optimum pH, i. e. the pH at which the overall risk of both colloidal and dissolved metal mobilization is minimized has to be worked out experimentally in these cases. This should also consider the option that metals might get mobilized in the topsoil but could be immobilized in deeper mineral horizons due to changing soil pH and soil composition.

### **7.3 Outlook**

With this study, I could demonstrate relevant processes of soluble and dispersible metal(loid) mobilization in the context of a liming-induced pH increase and in a drying event. However, the question which mechanism controls the mobilization in a scenario where both, liming and drying, occur simultaneously will remain a matter of debate: While my data in general suggests Ca to suppress colloid mobilization, Flury (2007) found, that the presence of a liquid-gas interface, which may form during the drying process, governs colloid stability. The author showed that if the colloid is attached to the liquid-gas interface, a high ionic strength solution containing Ca ions would not lead to the (according to the DLVO-theory) expected flocculation of colloids. However, if the colloid is attached to the solid-liquid interface, the same high ionic strength solution would induce the flocculation of colloids. These findings indicate that effects caused by drying could override effects caused by liming. Studies looking into the combination of both effects should therefore be the subject of future research.

My results suggest that the composition of the soil solid phase, i. e. the concentration of  $C_{org}$  and sesquioxide governs the mobilization of colloids as well as soluble and dispersible metal(loids) in the context of a drying and liming event.

However, since the number of samples is too small for the derivation of any general relation between the composition of the soil solid phase and mobilized colloidal metal(loid)s future studies should investigate more soils across a wider range of composition in order to gain a better understanding about the role of the composition of the soil solid phase not only in soluble but also in dispersible metal(loid) mobilization. In order to elucidate (im)mobilization mechanisms of As and Sb, future studies should address the role of the Ca cation in the interactions between As/Sb, DOM and Ca in defined systems. Up to now, numerous authors have raised speculations about how Sb could possibly be associated to different sorbents of the soil matrix, for instance by specific adsorption (Tighe et al, 2005) or organic complexation (Lyvén et al., 2003). However, only very few studies have clearly identified the binding mechanism (i. e. inner-sphere complexes on Fe-oxide surfaces; Scheinost et al., 2006). Since the knowledge about the type of bonding is crucial for the estimation of the mobilization potential more research should be directed towards the identification of Sb binding types to different sorbents of the soil.

To provide an estimate how much of the colloidal metal pool could potentially become available in the dissolved phase once the colloid has been translocated to a different environment, future research should investigate labile fractions of the metal(loid)s associated to the colloid.

A next step following the batch studies of this thesis should include experiments, which are conducted under more natural conditions in order to clarify the environmental relevance of the identified processes. This should eventually lead to the derivation of key parameters, which allow for the quantification of colloidal metal(loid)s that could potentially be leached from soil to groundwater.



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## Curriculum vitae

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- 1974            born on February 27<sup>th</sup> in Schorndorf (Germany)
- 1993            Graduation (Abitur) at Maria-Merian-Schule, Waiblingen (Germany)
- 1993-1994    Au-Pair in Great Britain
- 1994-1996    Technical College “Chemisches Institut Dr. Flad”, Stuttgart  
                  1996: “Staatsexamen”, Chemical-technical assistant
- 1996-1997    Internships in France (CEPHAC, Poitiers) and Great Britain  
                  (DeMontfort University, Leicester)
- 1997-2002    Study of Environmental Sciences at the Universities of Lüneburg, Trier  
                  and Tübingen
- 2002            Master of Science in Applied Environmental Geoscience, University of  
                  Tübingen
- 2003-2007    PhD student at the Department of Soil Science, Berlin University of  
                  Technology
- 2005            Research stay (7 months), CSIRO Land and Water, Adelaide, Australia  
                  - Size-fractionation of colloids by means of multi-stage tangential ultrafiltration  
                  - Bioavailability of heavy metals as indicated by diffusive gradients in thin films



# Appendix

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## Chapter 2: A method for the determination of hydrophobicity of suspended soil colloids

### Appendix 2.1: Hydrophobicity of differently treated goethite - DCM-method

#### P-treated goethite

pH	Zetapotential [mV]	Hydrophobicity		
		a	b	c
1.7	8.0	96.6%	96.2%	96.2%
4.0	0.4	96.3%	96.2%	96.6%
4.2	-2.8	95.5%	93.6%	95.1%
4.4	-11.0	96.4%	96.6%	97.2%
4.6	-4.9	71.6%	88.5%	n.a.
4.8	-4.0	81.8%	75.5%	n.a.
5.0	-21.1	27.9%	32.6%	32.1%
5.6	-26.3	6.7%	3.1%	16.1%
6.5	-29.6	9.0%	9.1%	9.1%
7.0	-33.9	6.9%	6.9%	6.9%
7.5	-34.5	10.8%	10.8%	10.8%
8.0	-33.5	29.3%	29.3%	29.4%

#### Al-treated goethite

2.0	37.5	52.0%	51.4%	55.0%
3.0	33.1	43.5%	43.9%	52.3%
4.0	35.3	42.1%	42.0%	41.8%
5.0	43.0	9.2%	10.0%	10.1%
6.1	34.0	26.7%	26.7%	26.3%
7.0	29.4	34.4%	34.3%	34.2%
7.5	25.7	67.1%	67.2%	67.2%
8.0	24.6	79.3%	79.3%	79.1%

#### Mg-treated goethite

2.0	43.8	16.0%	17.1%	16.9%
3.0	37.1	4.8%	5.9%	5.5%
4.0	32.3	16.3%	16.6%	16.5%
5.0	30.3	29.9%	30.2%	29.8%
6.0	26.3	31.7%	31.6%	31.1%
7.0	23.6	85.4%	85.0%	85.1%
8.0	8.0	38.0%	37.8%	37.4%

#### Na-treated goethite

2.2	37.0	17.4%	17.6%	17.7%
3.2	35.7	13.0%	13.8%	14.8%
4.1	34.5	4.3%	5.1%	5.1%
5.1	38.1	12.6%	12.6%	12.6%
6.1	26.9	17.2%	17.1%	17.3%
6.9	25.3	28.1%	28.2%	28.4%
8.1	5.1	58.8%	58.6%	58.8%

n. a.: data not available

## Appendix 2.2: Hydrophobicity of Al- and P-treated goethite - C18-method

### P-treated goethite

pH	Zetapotential [mV]	Hydrophobicity		
		a	b	c
3.8	1.8	55.2%	51.8%	55.5%
4.0	-7.5	40.8%	36.9%	39.3%
4.4	-8.2	31.3%	35.1%	38.3%
4.6	-13.3	2.3%	0.0%	2.0%
5.1	-19.7	4.9%	0.0%	0.0%
5.2	-23	4.7%	5.8%	5.0%
7.1	-33.5	0.9%	0.0%	2.0%

### Al-treated goethite

5.0	41.8	7.1%	11.1%	7.1%
5.8	37.6	6.6%	7.5%	11.0%
6.4	35.7	4.0%	6.2%	10.7%
7.0	30.2	15.2%	13.4%	13.0%
7.0	30.8	29.1%	n.a	n.a
7.2	27.8	51.5%	51.9%	51.9%

## Appendix 2.3: Capacity test of C18 microparticles

C18 [mg]	Hydrophobicity		
	a	b	c
10	61.1%	62.7%	60.7%
20	69.5%	61.0%	68.3%
30	71.3%	70.0%	63.8%
40	51.3%	71.0%	86.8%
50	77.3%	88.9%	85.0%
60	84.4%	85.4%	89.1%
70	83.4%	82.0%	82.4%
80	82.7%	88.6%	86.1%
100	90.3%	89.8%	92.9%
120	82.2%	68.4%	79.1%

## Appendix 2.4: Result of the comparison between goethite particles sorbed on DOC-treated and untreated C18 microparticles

Treatment	Hydrophobicity		
	a	b	c
Untreated	52.6%	48.9%	n.a.
DOC-20	50.4%	49.3%	59.7%
DOC-100	59.3%	65.7%	61.9%

n. a.: data not available

### Chapter 3: Hydrophobicity of soil colloids and heavy metal mobilization: Effects of drying

#### Appendix 3.1: Properties of soil suspensions and soil solid phase

Soil	Replicate	pH	EC [ $\mu\text{S m}^{-1}$ ]	Turbidity T1 [FNU]	Turbidity T2 [FNU]	Zeta potential [mV]	Particle size [nm]	Contact angle [°]
B1, moist	a	5.6	51.1	22.5	21.8	-18.0	550	84.4
	b	5.6	51.9	23.3	21.8	-17.9	300	85.4
	c	5.6	51.1	21.6	20.1	-17.8	380	85.9
B1, dried	a	6.1	54.7	18.1	15.4	-17.0	290	116.4
	b	6.0	57.1	14.6	14.5	-15.9	300	116.8
	c	5.9	55.5	9.64	9.70	-16.9	240	120.5
B2, moist	a	4.6	85.1	5.76	5.58	-16.3	280	83.7
	b	4.6	88.0	6.89	5.97	-15.9	600	83.9
	c	4.6	83.7	6.34	6.13	-15.9	300	83.6
B2, dried	a	5.1	86.5	18.1	16.6	-16.2	900	120.4
	b	4.9	87.0	7.96	7.73	-15.8	300	122.6
	c	5.0	84.1	7.50	n.a.	-16.4	300	120.7
B3, moist	a	5.5	93.4	10.5	10.2	-16.3	600	85.9
	b	5.4	97.6	9.49	8.81	-17.2	400	84.2
	c	5.5	118.7	7.71	7.78	-14.6	700	85.5
B3, dried	a	6.0	93.1	8.23	7.20	-15.9	n.a.	121.2
	b	5.6	97.8	8.01	n.a.	-16.5	290	121.7
	c	5.6	91.4	6.44	n.a.	-15.8	n.a.	127.5
TG, moist	a	4.2	768	0.98	n.a.	-5.9	n.a.	88.8
	b	4.0	760	1.36	n.a.	-1.6	n.a.	89.3
	c	4.0	753	1.21	n.a.	-2.9	n.a.	89.2
TG, dried	a	4.1	773	n.a.	n.a.	-5.9	n.a.	89.9
	b	4.2	722	0.47	n.a.	-4.4	550	90.0
	c	4.2	718	1.96	1.78	-7.2	n.a.	90.0
GS, moist	a	3.7	151.9	12.6	8.78	-17.4	n.a.	87.9
	b	3.7	156.1	4.80	4.80	-20.4	300	88.2
	c	3.7	157.3	2.68	2.51	-18.1	320	87.7
GS, dried	a	3.6	177.9	14.5	14.7	-16.4	800	110.8
	b	3.6	178.4	13.2	13.1	-17.5	350	111.2
	c	3.5	175.2	15.5	15.0	-17.8	300	107.5

n. a.: data not available

FNU: Formazin nephelometric unit

**Appendix 3.2a: Dissolved and colloidal concentrations in soil suspensions of field-moist and air-dried samples**

Soil	Replicate	DOC [mg l <sup>-1</sup> ]	COC [mg l <sup>-1</sup> ]	Cd <sub>diss</sub> [µg l <sup>-1</sup> ]	Cd <sub>coll</sub> [µg l <sup>-1</sup> ]	Zn <sub>diss</sub> [mg l <sup>-1</sup> ]	Zn <sub>coll</sub> [mg l <sup>-1</sup> ]
B1, moist	a	6.4	4.0	3.4	3.6	0.62	0.17
	b	5.8	3.8	3.9	4.2	0.61	0.11
	c	6.5	3.5	4.1	5.8	0.61	0.17
B1, dried	a	11.1	3.4	6.0	0.8	0.80	0.06
	b	11.5	3.0	6.2	0.8	0.74	0.07
	c	11.6	3.3	6.2	0.5	0.76	0.04
B2, moist	a	9.7	2.6	23.0	10.3	1.29	0.25
	b	8.5	2.9	22.8	10.3	1.18	0.24
	c	8.0	3.1	24.0	6.8	1.25	0.18
B2, dried	a	16.0	4.8	28.8	6.3	1.33	0.13
	b	15.5	4.1	29.1	5.2	1.29	0.12
	c	15.2	9.5	29.1	n.a.	1.31	n.a.
B3, moist	a	11.9	1.5	13.8	6.4	0.93	0.12
	b	9.9	3.5	15.0	8.3	0.99	0.14
	c	9.1	2.9	14.5	7.0	0.98	n.a.
B3, dried	a	15.2	4.1	17.4	1.9	0.95	0.04
	b	16.7	3.1	17.3	3.1	0.98	0.04
	c	16.2	2.8	17.5	2.1	0.9	0.0
TG, moist	a	8.7	2.2	17.3	5.8	0.73	0.06
	b	10.3	0.0	13.8	5.1	0.64	0.05
	c	7.8	2.1	13.0	4.7	0.58	0.05
TG, dried	a	17.1	6.1	14.8	1.5	0.55	0.04
	b	17.6	4.8	16.5	1.1	0.61	0.02
	c	17.3	4.9	15.6	2.4	0.61	0.03
GS, moist	a	19.6	5.8	1.3	1.4	below QL	below QL
	b	19.1	5.0	3.1	0.9	below QL	below QL
	c	20.4	3.9	2.0	0.1	below QL	below QL
GS, dried	a	38.2	7.2	0.7	0.5	below QL	below QL
	b	37.3	8.6	0.7	0.4	below QL	below QL
	c	39.7	7.8	0.7	0.3	below QL	below QL

DOC: dissolved organic carbon

COC: colloidal organic carbon

n. a.: data not available

QL: quantification limit

DL: detection limit

**Appendix 3.2b: Dissolved and colloidal concentrations in soil suspensions of field-moist and air-dried samples**

Soil	Replicate	Cu <sub>diss</sub> [µg l <sup>-1</sup> ]	Cu <sub>coll</sub> [µg l <sup>-1</sup> ]	Pb <sub>diss</sub> [µg l <sup>-1</sup> ]	Pb <sub>coll</sub> [µg l <sup>-1</sup> ]
B1, moist	a	70.9	28.6	2.1	42.3
	b	72.6	17.9	2.0	40.7
	c	73.9	62.6	n.a.	n.a.
B1, dried	a	208.3	n.a.	2.1	18.4
	b	186.1	n.a.	1.7	17.5
	c	179.2	n.a.	8.8	18.7
B2, moist	a	162.4	18.2	50.3	63.6
	b	173.4	0.0	18.5	48.3
	c	185.1	0.0	7.6	179.5
B2, dried	a	240.7	n.a.	n.a.	25.6
	b	239.4	39.4	9.6	20.5
	c	245.0	65.1	12.2	18.1
B3, moist	a	35.4	125.8	1.5	24.1
	b	70.4	266.3	0.0	29.3
	c	131.8	45.5	0.2	22.3
B3, dried	a	n.a.	n.a.	0.0	18.0
	b	226.6	45.0	1.8	12.0
	c	219.9	33.4	0.7	11.1
TG, moist	a	n.a.	n.a.	54.7	26.4
	b	52.0	100.3	58.5	26.4
	c	49.0	93.1	60.9	20.5
TG, dried	a	167.7	16.0	n.a.	n.a.
	b	166.2	12.6	84.7	16.5
	c	n.a.	n.a.	73.3	14.9
GS, moist	a	18.4	19.0	1348.8	351.5
	b	30.2	10.6	1098.0	426.2
	c	22.7	n.a.	1421.5	561.6
GS, dried	a	17.0	6.4	2564.6	662.6
	b	14.3	9.6	2675.6	537.2
	c	14.0	4.5	2756.4	471.9

n. a.: data not available

**Chapter 4: Increasing pH releases colloidal lead in a highly contaminated forest soil**

**Appendix 4.1: Total mobilized Pb concentration as a function of shaking time (soil 1; pH of soil suspension: 3.9)**

Time [h]	Mobilized Pb concentrations [mg l <sup>-1</sup> ]		
	a	b	c
2	0.8	1.1	0.8
4	1.3	1.5	1.3
8	1.4	1.6	1.7
24	1.5	1.5	1.6

**Appendix 4.2: Concentrations and properties of the soil suspensions (soil 1)**

pH	Replicate	Pb <sub>diss</sub>	Pb <sub>coll</sub>	DOC	COC
		[mg l <sup>-1</sup> ]			
pH 3	a	23.2	0.0	14.8	1.9
	b	22.4	0.0	14.7	0.9
	c	22.6	0.8	13.0	2.6
pH 4	a	2.0	1.7	32.2	24.0
	b	2.5	1.4	31.9	24.8
	c	2.0	1.6	31.8	25.1
pH 5	a	11.8	5.5	223.8	n.a.
	b	11.4	5.8	226.7	72.3
	c	11.2	5.7	224.6	69.6
pH 6	a	23.4	15.7	551.1	236.2
	b	24.5	16.7	545.7	296.8
	c	29.6	15.5	640.5	305.2
pH 7	a	51.0	58.5	1278.8	743.0
	b	41.2	61.3	1212.8	650.0
	c	50.5	53.5	1208.4	700.9

pH	Replicate	Optical Density	Zeta potential	Particle size	Fe <sub>coll</sub> *
		[-]	[mV]	[nm]	[mg l <sup>-1</sup> ]
pH 3	a	0.000	-16.6	400	-
	b	0.000	-12.5	500	-
	c	0.000	-14.0	n.a.	-
pH 4	a	0.062	-17.8	260	-
	b	0.065	-18.2	280	-
	c	0.050	-20.3	250	-
pH 5	a	0.342	-23.9	1025	0.23
	b	0.342	-23.0	600	0.52
	c	0.314	-23.5	350	0.15
pH 6	a	0.754	-28.5	n.a.	0.36
	b	0.778	-28.9	300	n.a.
	c	0.885	-26.6	300	0.42
pH 7	a	1.826	n.a.	1000	n.a.
	b	1.798	-36.9	1050	n.a.
	c	1.932	-32.7	600	3.1

\* concentration of colloidal residues, dissolved in 20 mL concentrated nitric acid  
 DOC: dissolved organic carbon; COC: colloidal organic carbon  
 n. a.: data not available

**Determination of the soil water content (105°C; soi l 1):**

Weight soil moist [g]	Weight soil dried [g]	Water loss
7.7224	4.226	54.70%

**Appendix 4.3: Concentrations and properties of the soil suspensions (soil 2)**

pH	Replicate	Pb <sub>diss</sub> [mg l <sup>-1</sup> ]	Pb <sub>coll</sub> [mg l <sup>-1</sup> ]	DOC [mg l <sup>-1</sup> ]	COC [mg l <sup>-1</sup> ]
pH 3.3	a	9.0	0.5	311.2	5.8
	b	n.a.	n.a.	n.a.	n.a.
	c	n.a.	n.a.	n.a.	n.a.
pH 4.8	a	11.5	20.5	504.0	236.4
	b	11.5	18.0	494.8	229.0
	c	n.a.	n.a.	n.a.	n.a.
pH 6.3	a	52.0	45.4	2422.0	337.0
	b	51.8	35.3	2539.0	311.0
	c	n.a.	n.a.	n.a.	n.a.

Ca(OH) <sub>2</sub>					
pH	Replicate	Pb <sub>diss</sub> [mg l <sup>-1</sup> ]	Pb <sub>coll</sub> [mg l <sup>-1</sup> ]	DOC [mg l <sup>-1</sup> ]	COC [mg l <sup>-1</sup> ]
pH 3.9	a	11.9	0.1	20.0	1.8
	b	11.8	0.0	19.3	2.1
	c	11.7	0.0	20.0	1.2
pH 5.2	a	1.3	0.0	49.9	2.2
	b	1.2	0.1	48.9	0.0
	c	1.2	0.1	54.3	0.0
pH 5.8	a	0.9	0.0	71.4	0.0
	b	0.7	0.1	72.9	0.0
	c	0.7	0.2	74.1	0.0
pH 6.9	a	1.7	0.9	173.9	7.4
	b	1.7	0.9	162.8	42.5
	c	1.7	0.4	166.1	36.1

KOH	Replicate	Turbidity [FNU]	Zeta potential [mV]	Particle size [nm]
pH 3.3	a	29.5	-11.3	963
	b	n.a.	n.a.	n.a.
	c	n.a.	n.a.	n.a.
pH 4.8	a	331.3	n.a.	464
	b	73.0	-16.1	n.a.
	c	n.a.	n.a.	n.a.
pH 6.3	a	n.a.	n.a.	n.a.
	b	n.a.	n.a.	n.a.
	c	n.a.	n.a.	n.a.

Ca(OH) <sub>2</sub>	Replicate	Turbidity [FNU]	Zeta potential [mV]	Particle size [nm]
pH 3.9	a	0.44	-3.7	1459
	b	0.63	-3.4	n.a.
	c	0.30	(-5.4)	n.a.
pH 5.2	a	0.20	-3.5	1879
	b	0.43	-3.3	1132
	c	0.68	-3.2	1458
pH 5.8	a	0.81	-1.6	820
	b	0.20	(1.1)	1132
	c	n.a.	-5.0	879
pH 6.9	a	8.47	-15.4	687
	b	n.a.	-13.3	1879
	c	8.30	-13.3	318

**Determination of the soil water content (105°C; soil 2):**

Weight soil moist [g]	Weight soil dried [g]	Water loss
1.90	1.15	39.5%

**Chapter 5: Lead, Antimony and Arsenic in dissolved and colloidal fractions from an amended shooting range soil as characterized by multi-stage tangential ultrafiltration and centrifugation**

**Appendix 5.1:**

**Data breakthroughcurve**

	Sample number	time [min]	volume [ml]	EC [mS cm <sup>-1</sup> ]
	1	0	5.193	64.83
Initial Solution:	2	30	4.636	56.38
0.5 M CaCl <sub>2</sub> ; EC: 66.03 mS cm <sup>-1</sup>	3	60	3.277	43.94
Rinsing solution:	4	90	3.280	35.44
0.01 M CaCl <sub>2</sub> ; EC: 2.15 mS cm <sup>-1</sup>	5	120	3.267	27.42
	6	150	3.211	23.340
	7	180	3.203	18.340
flow rate: 0.1 mL min <sup>-1</sup>	8	210	3.187	15.260
tangential flow: 20 mL min <sup>-1</sup>	9	240	3.216	12.510
	10	270	3.101	10.230
	11	300	3.148	7.880
	12	330	3.167	5.578
	13	360	3.178	4.483
	14	390	3.185	3.488
	15	420	3.110	2.744
	16	450	3.184	2.451
	17	480	3.154	2.233
	18	510	3.240	2.083
	19	540	3.271	2.130
	20	570	3.208	1.858
	21	600	3.073	2.135
	22	630	3.133	2.101
	23	660	3.115	2.035
	24	690	3.134	2.122
	25	720	3.195	2.112
	26	750	3.168	2.171
	27	780	3.071	2.075
	28	810	3.075	2.081
	29	840	2.890	2.100
	30	870	3.060	2.026
	31	900	3.060	2.101
	32	930	2.979	2.093
	33	960	3.143	2.081
	34	990	3.098	2.095
	35	1020	3.096	2.085
	36	1050	3.189	2.070
	37	1080	3.192	2.067
	38	1110	3.193	2.073
	39	1140	3.335	2.051
	40	1170	3.284	2.060
	41	1200	3.300	1.963
	42	1230	3.324	1.963
	43	1260	3.336	1.980
	44	1290	2.908	1.953
	45	1320	3.018	1.988
	46	1350	3.106	1.978
	47	1380	3.083	1.974
	48	1410	3.156	1.965

## Appendix 5.2: Concentrations in the individual MTUF chambers

<b>Blank</b>	<b>Volume</b>	<b>pH</b>	<b>EC</b>	<b>Mn</b>	<b>Fe</b>	<b>Al</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>Pb<sub>corr</sub></b>	<b>OC</b>
	<b>[ml]</b>		<b>[<math>\mu\text{S cm}^{-1}</math>]</b>					<b><math>\mu\text{g l}^{-1}</math></b>			<b>mg l<sup>-1</sup></b>
Initial solution	24.08	4.7	1430	744	159	n.d.	33	161	3172	n.d.	69.1
<b>Chambers:</b>											
1.2 $\mu\text{m}$ - 0.45 $\mu\text{m}$	2.48	4.2	1555	766	103	n.d.	30	160	2811	n.d.	106.5
0.45 $\mu\text{m}$ - 0.22 $\mu\text{m}$	2.42	4.1	1476	727	182	n.d.	30	151	2636	n.d.	100.5
0.22 $\mu\text{m}$ - 0.1 $\mu\text{m}$	2.56	4.1	1466	769	174	n.d.	32	157	2625	n.d.	111.3
0.1 $\mu\text{m}$ - 100 kDa	2.48	4.1	1477	780	135	n.d.	33	160	2708	n.d.	112.1
< 100 kDa	14.14	4.1	1473	714	126	n.d.	27	130	2675	n.d.	71.0
<b>KOH - A</b>											
	<b>Volume</b>	<b>pH</b>	<b>EC</b>	<b>Mn</b>	<b>Fe</b>	<b>Al</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>Pb<sub>corr</sub></b>	<b>OC</b>
	<b>[ml]</b>		<b>[<math>\mu\text{S cm}^{-1}</math>]</b>					<b><math>\mu\text{g l}^{-1}</math></b>			<b>mg l<sup>-1</sup></b>
Initial solution	22.29	6.5	1350	169	6788	n.d.	59	329	18470	18470	191.5
<b>Chambers:</b>											
1.2 $\mu\text{m}$ - 0.45 $\mu\text{m}$	2.27	6.4	1455	106	2128	n.d.	22	301	6556	9648	164.5
0.45 $\mu\text{m}$ - 0.22 $\mu\text{m}$	2.58	6.4	1413	96	1848	n.d.	20	271	6503	19421	180.4
0.22 $\mu\text{m}$ - 0.1 $\mu\text{m}$	2.74	6.3	1439	313	23288	n.d.	158	429	44873	56433	377.5
0.1 $\mu\text{m}$ - 100 kDa	2.36	6.4	1402	233	16396	n.d.	106	352	31000	31794	367.5
< 100 kDa	12.34	6.5	1446	94	1777	n.d.	20	267	6365	6365	187.2
<b>KOH - B</b>											
	<b>Volume</b>	<b>pH</b>	<b>EC</b>	<b>Mn</b>	<b>Fe</b>	<b>Al</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>Pb<sub>corr</sub></b>	<b>OC</b>
	<b>[ml]</b>		<b>[<math>\mu\text{S cm}^{-1}</math>]</b>					<b><math>\mu\text{g l}^{-1}</math></b>			<b>mg l<sup>-1</sup></b>
Initial solution	23.51	6.6	1311	142	6813	3448	47	208	15646	15646	445.4
<b>Chambers:</b>											
1.2 $\mu\text{m}$ - 0.45 $\mu\text{m}$	2.322	6.6	1252	91	2106	1356	17	176	6894	8408	463.48
0.45 $\mu\text{m}$ - 0.22 $\mu\text{m}$	2.568	6.7	1240	92	2119	1369	17	174	6931	9452	460.92
0.22 $\mu\text{m}$ - 0.1 $\mu\text{m}$	2.684	6.6	1387	290	20469	7900	138	283	37563	46817	704.6
0.1 $\mu\text{m}$ - 100 kDa	2.630	6.6	1410	210	13544	5381	87	231	29194	29612	637.28
< 100 kDa	13.306	6.7	1331	94	2004	1346	17	184	6844	6844	453.0

Pb<sub>corr</sub>: Pb associated with the filter membrane

OC: organic carbon

n.d.: not determined

## Pb concentrations of digested filter membranes

<b>Filter membrane</b>	<b><math>\mu\text{g l}^{-1}</math></b>	
	<b>A</b>	<b>B</b>
0.45 $\mu\text{m}$	703	352
0.22 $\mu\text{m}$	3173	635
0.1 $\mu\text{m}$	3018	2484
100 kDa	170	110

The filter membranes were digested in 10 ml concentrated HNO<sub>3</sub>.

## Appendix

<b>Ca(OH)<sub>2</sub> - A</b>	<b>Volume</b>	<b>pH</b>	<b>EC</b>	<b>Mn</b>	<b>Fe</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>Pb<sub>corr</sub></b>	<b>OC</b>
	<b>[ml]</b>		<b>[<math>\mu\text{S cm}^{-1}</math>]</b>			<b><math>\mu\text{g l}^{-1}</math></b>				<b>mg l<sup>-1</sup></b>
Initial solution	21.30	6.3	102	61	502	11	143	2137	2137	43.9
<b>Chambers:</b>										
1.2 $\mu\text{m}$ - 0.45 $\mu\text{m}$	2.28	6.2	104	54	256	10	150	917	3747	45.3
0.45 $\mu\text{m}$ - 0.22 $\mu\text{m}$	2.65	6.2	100	53	255	9	146	892	2857	37.8
0.22 $\mu\text{m}$ - 0.1 $\mu\text{m}$	2.21	6.3	101	56	311	10	145	1010	1608	57.5
0.1 $\mu\text{m}$ - 100 kDa	2.30	6.4	97	52	235	9	144	895	1190	59.4
< 100 kDa	11.86	6.4	94	52	246	9	142	924	924	52.7

<b>Ca(OH)<sub>2</sub> - B</b>	<b>Volume</b>	<b>pH</b>	<b>EC</b>	<b>Mn</b>	<b>Fe</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>	<b>Pb<sub>corr</sub></b>	<b>OC</b>
	<b>[ml]</b>		<b>[<math>\mu\text{S cm}^{-1}</math>]</b>			<b><math>\mu\text{g l}^{-1}</math></b>				<b>mg l<sup>-1</sup></b>
Initial solution	23.21	6.4	83	83	559	14	210	2503	2503	49.3
<b>Chambers:</b>										
1.2 $\mu\text{m}$ - 0.45 $\mu\text{m}$	2.45	6.0	92	70	319	11	186	1268	3585	52.5
0.45 $\mu\text{m}$ - 0.22 $\mu\text{m}$	2.68	6.0	96	64	284	10	179	1277	3510	49.0
0.22 $\mu\text{m}$ - 0.1 $\mu\text{m}$	2.44	6.0	95	72	624	12	191	1734	2712	60.9
0.1 $\mu\text{m}$ - 100 kDa	2.26	6.0	95	90	521	14	229	1441	1598	66.6
< 100 kDa	13.37	6.1	90	65	299	11	186	1312	1312	46.9

Pb<sub>corr</sub>: Pb associated with the filter membrane

OC: organic carbon

### Pb concentrations of digested filter membranes

Filter membrane	$\mu\text{g l}^{-1}$	
	<b>A</b>	<b>B</b>
0.45 $\mu\text{m}$	64.5	56.83
0.22 $\mu\text{m}$	49.6	59.94
0.1 $\mu\text{m}$	13.2	23.89
100 kDa	6.8	3.515

The filter membranes were digested in 10 ml concentrated HNO<sub>3</sub>.

### Determination of the soil water content (105°C):

Weight soil moist [g]	Weight soil dried [g]	Water loss
0.742	0.536	27.8%
1.023	0.751	26.6%

## Appendix 5.3: Concentrations in the centrifugates

Blank	Fe		As		Sb		Pb		organic C	
	a	b	a	b	a	b	a	b	a	b
			$\mu\text{g l}^{-1}$						$\text{mg l}^{-1}$	
Total	308	370	54	53	285	291	3.6	3.8	37.5	36.8
< 0.45 $\mu\text{m}$	299	299	52	53	282	282	3.6	3.8	37.1	37.2
< 0.22 $\mu\text{m}$	282	410	52	54	285	286	3.7	3.8	37.2	36.3
< 0.1 $\mu\text{m}$	288	385	53	52	273	278	3.6	3.5	37.8	36.4
< 0.009 $\mu\text{m}$ (100 kDa)	260	283	52	54	274	279	3.5	3.9	36.8	36.4

KOH	Fe		As		Sb		Pb		organic C	
	a	b	a	b	a	b	a	b	a	b
			$\mu\text{g l}^{-1}$						$\text{mg l}^{-1}$	
Total	4000	3400	50	49	706	659	8.4	7.6	138.8	124.4
< 0.45 $\mu\text{m}$	3900	3400	50	48	654	651	8.4	7.5	130.8	123.0
< 0.22 $\mu\text{m}$	3700	3400	47	44	647	670	8.4	7.5	130.9	123.1
< 0.1 $\mu\text{m}$	3600	3300	43	44	700	642	8.4	7.8	130.6	125.9
< 0.009 $\mu\text{m}$ (100 kDa)	2600	2300	40	37	660	629	7.7	7.1	126.6	121.2

Ca(OH) <sub>2</sub>	Fe		As		Sb		Pb		organic C	
	a	b	a	b	a	b	a	b	a	b
			$\mu\text{g l}^{-1}$						$\text{mg l}^{-1}$	
Total	778	799	21	18	396	395	2.7	2.7	86.2	84.5
< 0.45 $\mu\text{m}$	743	759	18	19	394	405	2.5	2.6	82.3	82.9
< 0.22 $\mu\text{m}$	714	733	19	18	405	407	2.6	2.5	82.2	82.7
< 0.1 $\mu\text{m}$	662	669	18	17	400	399	2.5	2.5	81.9	82.8
< 0.009 $\mu\text{m}$ (100 kDa)	590	524	14	16	379	387	2.4	2.4	83.0	81.2

## Determination of the soil water content (105°C):

Weight soil moist [g]	Weight soil dried [g]	Water loss	
0.490	0.376	28.5%	KNO <sub>3</sub> treatment
0.85	0.65	23.5%	KOH/Ca(OH) <sub>2</sub> treatment

**Appendix 5.4: Physico-chemical properties of the total solutions and centrifugates**

Total	pH		EC [ $\mu\text{S cm}^{-1}$ ]	
	a	b	a	b
Blank	4.6	4.6	1291	1294
KOH	6.6	6.6	658	656
Ca(OH) <sub>2</sub>	6.7	6.7	92.8	94.7

Blank	Turbidity [FNU]		Zeta potential [mV]		Particle size [nm]	
	a	b	a	b	a	b
Total	0.79	1.18	-14.5	-11.5	303	287
< 0.45 $\mu\text{m}$	0.59	0.83	-9.4	-8.1	334	319
< 0.22 $\mu\text{m}$	0.45	0.52	-2.2	-4.2	334	303
< 0.1 $\mu\text{m}$	0.26	0.34	2.0	1.1	458	319
< 0.009 $\mu\text{m}$ (100 kDa)	0.16	0.15	2.9	0.7	1132	1879

KOH	Turbidity [FNU]		Zeta potential [mV]		Particle size [nm]	
	a	b	a	b	a	b
Total	17.20	8.72	-24.9	-28.9	682	687
< 0.45 $\mu\text{m}$	8.64	6.82	-25.0	-29.5	272	303
< 0.22 $\mu\text{m}$	5.64	4.06	-23.2	-23.5	319	708
< 0.1 $\mu\text{m}$	1.57	1.50	-10.9	-10.5	339	274
< 0.009 $\mu\text{m}$ (100 kDa)	0.33	0.46	3.0	1.2	879	1132

Ca(OH) <sub>2</sub>	Turbidity [FNU]		Zeta potential [mV]		Particle size [nm]	
	a	b	a	b	a	b
Total	7.17	6.06	-15.9	-15.9	319	319
< 0.45 $\mu\text{m}$	4.34	5.21	-17.4	-17.1	192	654
< 0.22 $\mu\text{m}$	2.77	2.53	-13.7	-11.3	192	303
< 0.1 $\mu\text{m}$	0.88	0.99	-6.9	-2.4	319	319
< 0.009 $\mu\text{m}$ (100 kDa)	0.26	0.26	-2.6	2.2	n.a.	879

n.a.: not available

## Chapter 6: Mobilization of colloidal and dissolved Pb, As and Sb in a polluted, organic-rich soil – effects of pH increase and counterion valency

### Appendix 6.1: Properties of soil suspensions

KOH	Replicate	pH	EC [ $\mu\text{S cm}^{-1}$ ]	Turbidity [FNU]	Zeta potential [mV]	Particle size [nm]	
	pH 3.5	a	3.5	3680	1.01	-13.0	980
		b	3.6	3470	2.37	-14.3	879
		c	3.5	3600	1.82	-13.3	682
	pH 4.3	a	4.3	1324	5.82	-20.5	319
		b	4.3	3210	9.65	-19.5	524
		c	4.3	3180	5.25	-21.2	319
	pH 6.2	a	6.2	2190	13.3	-20.0	1083
		b	6.1	2170	9.9	-18.2	625
		c	6.3	2170	18.2	-18.4	536
pH 7.1	a	7.0	1457	30.16	-34.0	682	
	b	7.1	1472	40.00	-34.5	2137	
	c	7.2	1467	(9.3)	-35.2	319	

Ca(OH) <sub>2</sub>	Replicate	pH	EC [ $\mu\text{S cm}^{-1}$ ]	Turbidity [FNU]	Zeta potential [mV]	Particle size [nm]	
	pH 3.7	a	3.6	1277	0.99	-3.1	100
		b	3.6	1264	1.41	-6.2	879
		c	3.8	1236	1.85	-3.7	n.a.
	pH 4.4	a	4.4	842	0.78	(-10.4)	1523
		b	4.4	832	0.93	-3.4	842
		c	4.4	829	0.63	-2.2	682
	pH 5.3	a	5.3	333	3.79	-12.8	446
		b	5.3	327	3.56	-12.1	682
		c	5.3	325	(1.75)	-10.3	682
pH 6.1	a	6.1	53.2	16.7	-18.7	853	
	b	6.1	54.9	12.5	-18.0	651	
	c	6.2	56.8	13.6	-18.9	808	
pH 6.7	a	6.7	84.5	11.9	-15.7	334	
	b	6.7	79.5	16.1	-15.9	319	
	c	6.6	76.1	11.5	-16.7	319	

n. a.: data not available

FNU: Formazin nephelometric unit

## Appendix

<b>KOH</b>	<b>Replicate</b>	<b>Pb<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>Pb<sub>coll</sub></b> [µg l <sup>-1</sup> ]	<b>As<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>As<sub>coll</sub></b> [µg l <sup>-1</sup> ]	<b>Sb<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>Sb<sub>coll</sub></b> [µg l <sup>-1</sup> ]
pH 3.5	a	600	0.0	29.9	0.0	8.7	0.1
	b	550	0.0	18.0	0.0	4.1	0.0
	c	550	200	17.1	0.0	3.0	0.3
pH 4.3	a	500	350	19.2	2.1	7.4	0.0
	b	450	300	17.7	3.9	5.3	0.0
	c	(1100)	0	(32.3)	0.0	(21.3)	0.0
pH 6.2	a	4250	650	36.7	2.9	21.9	0.0
	b	2950	400	30.8	1.9	20.9	0.0
	c	3700	500	28.2	1.6	12.4	0.0
pH 7.1	a	5250	1050	48.9	7.3	25.0	0.0
	b	4800	700	39.9	4.6	17.5	0.3
	c	4300	500	38.4	2.6	20.4	0.0

<b>Ca(OH)<sub>2</sub></b>	<b>Replicate</b>	<b>Pb<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>Pb<sub>coll</sub></b> [µg l <sup>-1</sup> ]	<b>As<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>As<sub>coll</sub></b> [µg l <sup>-1</sup> ]	<b>Sb<sub>diss</sub></b> [µg l <sup>-1</sup> ]	<b>Sb<sub>coll</sub></b> [µg l <sup>-1</sup> ]
pH 3.7	a	254.7	(59.7)	13.0	0.3	3.0	0.0
	b	297.0	0.0	15.5	0.5	3.4	0.0
	c	238.2	1.5	15.2	0.0	2.0	0.0
pH 4.4	a	73.5	0.0	16.3	0.0	3.3	0.0
	b	74.5	0.0	13.8	0.0	1.7	0.3
	c	73.1	0.0	15.9	0.0	2.0	0.2
pH 5.3	a	43.0	10.0	9.8	0.8	2.6	0.0
	b	43.8	6.9	10.0	0.4	2.7	0.0
	c	39.2	6.9	10.7	1.0	3.2	0.0
pH 6.1	a	95.8	27.6	7.9	0.1	6.4	0.0
	b	111.9	35.3	7.4	0.2	5.3	0.0
	c	102.2	(160.7)	7.7	0.3	5.3	0.1
pH 6.7	a	95.8	27.6	7.9	0.1	6.4	0.0
	b	111.9	35.3	7.4	0.2	5.3	0.0
	c	102.2	(160.6)	7.7	0.3	5.3	0.1

## Appendix

KOH	Replicate	DOC [mg l <sup>-1</sup> ]	COC [mg l <sup>-1</sup> ]	Fe <sub>diss</sub> [µg l <sup>-1</sup> ]	Fe <sub>coll</sub> [µg l <sup>-1</sup> ]
pH 3.5	a	19.4	1.0	106.6	0.0
	b	18.4	1.6	102.6	33.2
	c	19.0	1.9	90.4	(759.1)
pH 4.3	a	52.6	16.4	417.5	108.5
	b	50.5	21.7	477.6	166.2
	c	51.3	10.9	(197.1)	242.6
pH 6.2	a	605.5	104.6	6535.5	665.7
	b	441.1	n.a.	4219.0	(366.7)
	c	462.6	n.a.	4163.5	545.6
pH 7.1	a	1034.2	136.8	9024.0	762.3
	b	834.2	170.4	6605.0	(2188.9)
	c	703.6	289.0	5414.9	991.4

Ca(OH) <sub>2</sub>	Replicate	DOC [mg l <sup>-1</sup> ]	COC [mg l <sup>-1</sup> ]	Fe <sub>diss</sub> [µg l <sup>-1</sup> ]	Fe <sub>coll</sub> [µg l <sup>-1</sup> ]
pH 3.7	a	17.9	1.0	(54.0)	6.2
	b	16.2	1.4	19.6	(25.1)
	c	15.4	1.1	22.4	10.0
pH 4.4	a	20.2	1.9	7.9	30.9
	b	21.6	1.8	8.2	38.1
	c	20.3	2.1	8.8	27.4
pH 5.3	a	33.1	(3.4)	70.3	10.3
	b	34.2	1.2	74.1	3.3
	c	34.2	1.6	71.4	0.0
pH 6.1	a	62.4	5.4	251.5	32.4
	b	62.4	2.7	252.3	36.0
	c	66.0	0.8	241.7	49.0
pH 6.7	a	62.4	5.4	0.0	0.0
	b	62.4	2.7	0.0	0.0
	c	66.0	(0.75)	0.0	4.3

### Determination of the soil water content (105°C):

Weight soil moist [g]	Weight soil dried [g]	Water loss	
1.20	0.88	26.70%	KOH treatment
0.92	0.64	30.40%	Ca(OH) <sub>2</sub> treatment