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Philosophiae Doctor (PhD), Thesis 2016:71

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Faculty of Environmental Science and Technology
Department of Environmental Science

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To my husband Simen

and children

Ida, Silje, and Andreas

Wisdom is not a product of schooling but of the lifelong attempt to acquire it

-Albert Einstein.

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Summary

In recent years there has been an increasing interest for the use of crushed minerals and rocks as soil amendment and slow-release fertilizers in agriculture. Apatite-biotite-carbonatite (short form: carbonatite) rock from the Lillebukt Alkaline Complex (LAC), located at Stjernøy, Northern Norway, contains significant amounts of essential nutrients like calcium (Ca), potassium (K), magnesium (Mg), and phosphorus (P), all in minerals that weather quite easily. The main minerals are calcite (42 wt%), biotite (30 wt%), apatite (7.5 wt%) and some nepheline. Weathering of the carbonatite may supply nutrients to soil in closer agreement with the plants demand than easily soluble mineral fertilizers. However, large amounts are needed in order to achieve the desired fertilizing effect. This practice may alter the content of potentially harmful elements in the soil. Barium (3.2 g Ba kg^{-1}) enriched in the carbonatite may cause undesired uptake to plants when applied to agroecosystems. Prior to assess the agro-ecological risk when considering the carbonatite rock for farming practices, an investigation of the plant availability of Ba from the carbonatite rock powder is requisite. Thus, the present work target to gain new knowledge on factors influencing the geochemistry of Ba in soils with ordinary and Ba-enriched mineralogy, with particular focus on the carbonatite rock, and the availability of Ba to plants under observational and experimental conditions.

A survey of the vegetation at Stjernøy demonstrated a great interspecies variation in Ba concentration, which was closely related to the plants affinity for Ca (Paper I). Low median concentrations and transfer factor (TF) for Ba in grasses (30 mg kg^{-1}, TF: 0.06 – 2.1), intermediate in dwarf shrubs (100 mg kg^{-1}, TF: 0.4 - 8) and higher in herbs (150 mg kg^{-1}, TF: 0.4 -17) were observed. In general, Ba in vegetation was equally high or higher compared to values commonly reported in vegetation in northern part of Europe and Russia. Most plants did neither accumulate Ba nor reflect the soil mineralogy at Stjernøy. One exception was the leguminous species *Vicia cracca* L. (bird vetch) that accumulated Ba up to 2 g kg^{-1} in average, closely reflecting the bedrock and soil chemistry, and exceeding plant Ba concentrations reported to induce phytotoxicity in other herbaceous species.

Cultivation of agricultural plant species in pot experiments was conducted in order to test potential antagonistic effects of liming ($CaCO_3$, Paper II) and peat organic matter (OM, Paper III) on the mobilization of Ba from soil minerals, and the corresponding Ba uptake to plants. In the first pot experiment (Paper II), nine agricultural plants were cultivated in an aeolian

sandy soil dominated by tectosilicates. All the species were able to acquire Ba from the sparingly soluble feldspars in the soil, and Ba was closely related to Ca concentration in plants. Barium concentrations and TFs were lowest in shoots of the grass species *Festuca arundinácea* L. (tall fescue, 110 mg kg^{-1}, TF: 6), and highest in the legumes *Trifolium repens* L. (white clover, 500 mg kg^{-1}, TF: 22) and bird vetch (600 mg kg^{-1}, TF: 25). A significant decrease in Ba uptake by liming ($CaCO_3$) was observed in plants with low affinity for Ca uptake, e.g. tall fescue. Plants with high affinity for Ca accumulated the most Ba in shoots, e.g. bird vetch, and no antagonistic effect by liming on Ba concentration was observed. The low cation exchange capacity (CEC), organic matter (OM), and sulfate content, resulted in a low element retention potential of the sandy soil that probably facilitated direct absorption of exchangeable Ba to plants. This caused Ba to concentrate in white clover and bird vetch up to concentrations reported to cause phytotoxicity in other herbaceous species.

In the second pot experiment (Paper III and IV), carbonatite rock powder was added as lime and nutrient supply to the sandy soil mixed with various amounts of peat, and correlated with uptake of Ba, Sr, Ca, Mg and K to tall fescue and white clover. The main findings showed that carbonatite supply to soil increased Ba uptake by test crops significantly, and Ba was closely associated with the Ca content in plants (Paper III). The mobilization and uptake of Ba to plants from carbonatite rock powder increased on additional supply of peat, probably due to enhanced weathering of carbonatite and feldspar minerals by organic acids, which amplified the exchangeable Ba fraction in soil. In combination with the pot experiment in Paper III, Ba speciation in soil and pore water was determined using diffusive gradients in thin films technique (DGT) and WHAM/Model VI (Paper IV). Plants took up Ba mainly from exchangeable sites in soil, as well as Ba bound diffusely to colloids in pore water. This exemplifies that Ba might be relatively mobile in soils despite the adsorption to peat organic matter. The DGT measurements showed that white clover mobilized Ba more effectively from soil than tall fescue. This was also reflected in the plants, with average Ba concentration ranging from 13 to 50 mg kg^{-1} in tall fescue (TF: 0.9 – 2), and 18 to 90 mg kg^{-1} in white clover (TF: 0.8 – 3). In addition, this indicates an active plant factor in the rhizosphere, and a species dependent Ba acquisition potential. The significantly lower Ba uptake of comparable plants in control soils of the second pot experiment compared to the first pot experiment was probably an effect of Ba precipitation with sulfate applied as nutrient solutions in the second pot experiment.

The potential toxicity of Ba in plants grown on carbonatite, or carbonatite-amended soils are still unexplored. However, the relatively moderate Ba uptake by most plants grown on soils with ordinary and Ba enriched mineralogy presented in the thesis, accompanied by findings in the current literature, is promising when considering carbonatite application to soils as a lime and slow-release fertilizer. Barium mobility and bioavailability appear to be primarily controlled by e.g. organic acid content, cation exchange capacity, sulphate content, and rhizosphere activity in mineral soils, as well as plant characteristics. The present work shows the importance of investigating different groups of vascular plants due to interspecies differences in Ba acquisition potential and distribution strategies. A potential cause of concern that should be investigated in field trials, address to the carbonatite application to highly degraded mineral soils, or soils with high contents of organic acids and little sulphur (S), as Ba may accumulate in certain plant species with particular demand for Ca, and/or high acquisition potential for Ba.

Sammendrag

I de senere år har interessen for bruk av steinmel som gjødsel i jordbruket økt. Apatitt-biotitt-karbonatitt (her kalt karbonatitt) fra det alkalinske komplekset i Lillebukt er lokalisert på Stjernøy i Nord-Norge, og inneholder signifikante mengder av essensielle plantenæringsstoffer som kalsium (Ca), kalium (K), magnesium (Mg) og fosfor (P), alle i bergarter som forvitrer lett. Hovedmineralene er kalsitt (42 vekt%), biotitt (30 vekt%), apatitt (7.5 vekt%), i tillegg til noe nefelin. Forvitring av karbonatitt vil kunne tilføre næringsstoffer til jorden mer tilpasset plantenes næringsbehov, i forhold til lettløselige mineralsalter. Det er derfor nødvendig med større mengder steinmel for å oppnå den ønskede gjødslingseffekten. Dette kan føre til en økt mengde av mindre ønskelige grunnstoffer i jord. I karbonatitt-steinmel utgjør de anrikede mengdene av barium (Ba) en mulig risiko dersom karbonatitt tilføres jordbruksjord. Før man kan vurdere den agroøkologiske risikoen ved å bruke karbonatitt-steinmel som gjødsel i landbruk, har det vært nødvendig å undersøke plantetilgjengeligheten av Ba fra karbonatitt-steinmel. Hovedhensikten med dette arbeidet var å øke kunnskapen om faktorer som påvirker geokjemien av Ba i jord med ordinær og Ba-anriket mineralogi, der karbonatitt-steinmelet var spesielt i fokus. Barium-tilgjengeligheten til planter ble undersøkt både i et observasjonsstudie i felt, samt under eksperimentelle forhold.

Et feltstudiet på Stjernøy viste en stor variasjon i Ba-konsentrasjon i de ulike planteartene. Barium-konsentrasjonen var sterkt korrelert med plantenes Ca-opptak (Paper I). Mediankonsentrasjonen og overføringsfaktoren (TF) av Ba var lav i gressarter (30 mg kg^{-1}, TF: 0.06 – 2.1), middels i buskvekster (100 mg kg^{-1}, TF: 0.4 - 8), og høyest i urteplanter (150 mg kg^{-1}, TF: 0.4 -17). Generelt var Ba-konsentrasjonen i vegetasjonen like høy, eller høyere sammenliknet med Ba i vegetasjon i nordlige deler av Europa og Russland. De fleste plantene på Stjernøy hverken akkumulerte Ba, eller reflekterte jordmineralogien. Et unntak var belgveksten *Vicia cracca* L. (fuglevikke), som akkumulerte Ba opp til 2 g kg^{-1} i gjennomsnitt. Barium-konsentrasjonen i denne arten gjenspeilte både berggrunns- og jordmineralogien, og Ba-nivåene oversteg konsentrasjoner som har blitt rapportert å forårsake toksiske symptomer i andre belgvekster.

De potensielle antagonistiske effektene av kalking ($CaCO_3$, Paper II), og organisk materiale i form av torv (Paper III og IV) i forhold til mobilisering av Ba fra mineraljord, og det påfølgende Ba-opptaket i planter ble undersøkt i potteforsøk. I det første potteforsøket (Paper II) ble ni jordbruksplanter dyrket i en flygesand dominert av tektosilikater. Alle planteartene

tok opp Ba fra feltspatmineralene i sanden, og Ba-konsentrasjonen korrelerte sterkt med Ca-konsentrasjonen i plantene. Både konsentrasjonen av Ba og TF var lav i de overjordiske plantedelene til gressarten *Festuca arundinácea* L. (strandsvingel, 110 mg kg^{-1}, TF: 6), og høyest i belgvekstene *Trifolium repens* L. (hvitkløver, 500 mg kg^{-1}, TF: 22) og fuglevikke (600 mg kg^{-1}, TF: 25). Ved kalking ble det målt en betydelig reduksjon i Ba-opptak i planter med lav affinitet for Ca, blant annet strandsvingel. Planter med høyere affinitet for Ca, som fuglevikke, akkumulerte mest Ba i overjordiske plantedeler, og ingen antagonistisk effekt av kalking på Ba-konsentrasjon ble observert. Lav kationbyttekapasitet, lavt innhold av organisk materiale og sulfat førte til lavt retensjonspotensiale i sanden, noe som antagelig favoriserte direkte planteopptak av utbyttbart Ba. Dette førte til at Ba akkumulerte i hvitkløver og fuglevikke til konsentrasjoner som er rapportert å gi toksiske symptomer i andre urteplanter.

I det andre potteforsøket (Paper III og IV) ble karbonatitt-steinmel tilført som kombinert kalkings- og gjødslingsmiddel til sand blandet med ulike mengder torv. Jordblandingene ble så korrelert med opptak av Ba, Sr, Ca, Mg og K i strandsvingel og hvitkløver. Hovedfunnene viste at karbonatitten økte Ba-opptaket i plantene betydelig, og Ba korrelerte sterkt med Ca-opptaket i plantene (Paper III). Mobiliseringen og planteopptaket av Ba fra karbonatitten økte med økende mengde torv, sannsynligvis som følge av at organiske syrer i torv fremmet forvitringen av karbonatitt- og feltspatmineraler. Dette førte til en økt mengde utbyttbart Ba i jord. Relatert til potteforsøket i Paper III, ble Ba speciering i jord og porevann bestemt ved bruk av «diffusive gradients in thin films» (DGT) og WHAM/Model VI (Paper IV). Plantene tok opp Ba hovedsakelig fra utbyttbare sider i jord, samt Ba som var diffust bundet til kolloider i porevannet (Paper IV). Dette viste at Ba kan være relativt mobilt i jord selv om Ba er adsorbert til organisk materiale i form av torv. DGT-målingene viste at hvitkløver mobiliserte Ba mer effektivt fra jord i forhold til strandsvingel. Dette ble også reflektert i plantene, der gjennomsnittlig Ba-konsentrasjon varierte fra 13 til 50 mg kg^{-1} i strandsvingel (TF: 0.9 – 2), og fra 18 til 90 mg kg^{-1} i hvitkløver (TF: 0.8 – 3). Dette antyder en aktiv innflytelse av plantene i rhizosfæren, og et artsavhengig potensial for Ba-opptak. Ved å se på sammenliknbare plantearter i kontrolljord i det andre potteforsøket sammenliknet med det første potteforsøket, var det et betydelig lavere Ba-opptak i det andre potteforsøket. Dette var sannsynligvis et resultat av Ba-utfelling med sulfat, fordi det ble tilsatt sulfat i næringsløsningene i det andre potteforsøket.

Toksiske symptomer forårsaket av Ba i planter som vokser i karbonatitt, eller jord tilsatt karbonatitt har ikke blitt undersøkt. Likevel viser dette studiet at de fleste planteartene som vokser i jord med ordinær og Ba-anriket mineralogi, har relativt moderat Ba-opptak sammenliknet med nivåer som er oppgitt i litteraturen. Dette er lovende med tanke på bruk av karbonatitt som et kalkings- eller gjødslingsprodukt. Mobiliteten og biotilgjengeligheten av Ba ser ut til å primært være styrt av mineraljordens innhold av organiske syrer, kationbyttekapasitet, sulfatinnhold og rhizosfæreaktivitet, i tillegg til planten selv. Dette studiet viser viktigheten av å undersøke ulike grupper av vaskulære planter, fordi ulike plantearter viser forskjellig evne til å ta opp og transportere Ba. Et potensielt problem som bør undersøkes nærmere i felt, er tilførsel av karbonatitt til svært forvitret mineraljord, eller jord med høyt innhold av organiske syrer og lite svovel, fordi Ba muligens kan akkumulere i noen planter med spesielt stort behov for Ca, eller planter som viser potensiale for Ba-akkumulasjon.

List of original papers

The present thesis is based on the following papers and will be referred to in the text by the Roman numerals:

(I) Myrvang, M. B., Hillersøy, M. H., Heim, M., Bleken, M., Gjengedal, E (2016). Uptake of macronutrients, barium and strontium to vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway. J. *Plant Nutr. Soil Sci.* Accepted on the 18th of August. Scheduled for issue 6/2016. DOI: 10.1002/jpln.201600328.

(II) Myrvang, M. B., Bleken, M. A, Krogstad, T., Heim, M., Gjengedal, E (2016): Can liming reduce barium uptake by agricultural plants grown on sandy soil? *J. Plant Nutr. Soil Sci.* 179 (4), 557-565. DOI: 10.1002/jpln.201600104.

(III) Myrvang, M. B., Heim, M., Krogstad, T., Almås, Å. R., Gjengedal, E. Use of carbonatite rock as fertilizer and liming agent, and uptake of Ba, Sr, Ca, Mg and K to *Festuca arundinácea* and *Trifolium repens* on increasing supply of peat. *J. Plant Nutr. Soil Sci*. Accepted with minor revisions on the 7th of November, 2016.

(IV) Myrvang, M. B., Gjengedal, E., Heim, M., Krogstad, T., Almås, Å. R. (2016): Geochemistry of barium in soils supplied with apatite-biotite-carbonatite rock powder and barium uptake to plants. *Applied Geochemistry*. 75, 1-8. DOI: http://dx.doi.org/10.1016/j.apgeochem.2016.10.013.

Abbreviations and definitions

Accumulation	Higher element concentration, in this context in plants compared to that of the soil
ATSDR	Agency of Toxic Substances and Decease Registry
Ba_{dfa}	Diffusely bound barium to colloidal fulvic acids in pore water
Ba_{dgt}	Barium concentration estimated by the Diffusive Gradients in Thin Films Technique
Ba_{exc}	Exchangeable barium
Ba_{fa}	Barium bound to colloidal fulvic acids (FA) in pore water
Ba_{pw}	Barium in pore water
Ba_{upt}	Barium uptake to plants
BCF	Bio Concentration Factor
CEC	Cation Exchange Capacity
DGT	Diffusive Gradients in Thin Films Technique
DOC/TOC	Dissolved Organic Carbon/Total Organic Carbon
EF	Enrichment Factor
HNO_3	Nitric acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductive Coupled Plasma Optical Emission Spectrometry
LAC	Lillebukt Alkaline Complex
LO(A)EC	Lowest Observed (Adverse) Effect Concentration
LO(A)EL	Lowest Observed (Adverse) Effect Level
LOD	Limit of detection
LOQ	Limit of quantification
RC	Relative Contribution
SIP	Seiland Igneous Province
SOM	Soil Organic Matter
TI	Translocation Index
TOC	Total Organic Carbon
TF	Transfer Factor
PD	Plant Distribution
USEPA	United States Environmental Protection Agency
WHAM	Windermere Humic Aqueous Model for speciation of elements
WHO	World Health Organization
XRF	X-ray fluorescence

Table of Content

Paper I-V has individual page numbering.

1 Introduction

The present study focuses on gaining new knowledge on the basic mechanisms related to the geochemistry and mobilization of Ba in soil-plant systems, subsequently Ba availability and uptake to vascular plants under observational and experimental conditions. The main source of Ba in focus originates from apatite-biotite-carbonatite (short form: carbonatite), a rock applied in crushed form that has a potential as soil amendment or rock fertilizer in agriculture. The carbonatite is part of the Lillebukt Alkaline Complex (LAC), situated at Stjernøy, Northern Norway. Different compartments, i.e. bedrock, soil, pore water and selected vascular plants has been selected for this purpose. The approaches employed to address the fate and behavior of Ba in mineral soils and plant samples are presented in the thesis.

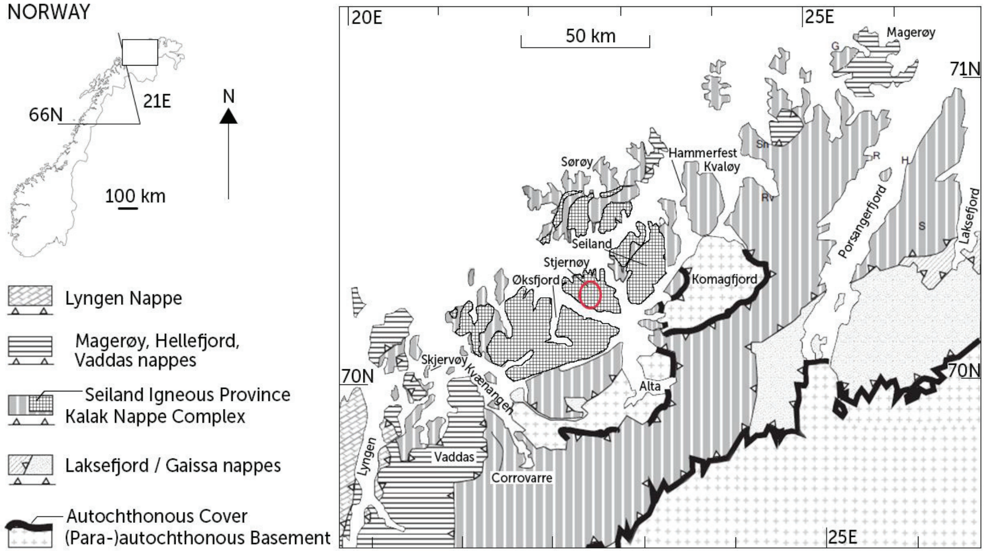
Chapter 1 gives an introduction to the agricultural use of crushed whole rock (rock powder) from the LAC and its mineralogy, the potentials and obstacles regarding this multinutrient fertilizer, and the thesis' objectives, expectations and hypotheses. The theoretical background and the current knowledge on Ba, the investigated parameters and approaches used to assess the geochemistry and availability of Ba are presented in Chapter 2. The problem formulation, identification of potential hazards, description of the field survey and experiments, methodologies and measurement techniques are provided in Chapter 3. A summary of the scientific papers, discussion of main results, and implications of the study findings are presented in Chapter 4 and 5. The conclusions and recommendations are given in Chapter 6.

1.1 Fertilization of soil in agriculture

Soil is the primary growth medium for plants. Soils provide physical support, a steady supply of inorganic nutrients and water, and gives a suitable gaseous environment for the root system (Raven et al. 1999). Inorganic nutrients derived from the atmosphere and from weathering of rocks and minerals are the essential sources of macro- and micronutrients required by higher plants. Under natural climatic conditions, the provision of nutrients to annual crop production by physical and chemical weathering of minerals is insufficient. To prevent soil fertility decrease due to imbalance between soil nutrient loss and gain, replenishment of nutrients that have been removed or lost is essential (Van Straaten 2002). Fertilizers are defined by Finck (1982) as "substances intended to be supplied directly or indirectly to crops in order to promote their growth, increase their yields, or improve their quality". For optimal crop production, most commercial farming practices in the world rely on either organic or agrochemical nutrient inputs, or a combination of organic and inorganic nutrient inputs (Van Straaten 2006). Natural fertilizers (e.g. poultry, cattle manure, leaf litter, sludge, ashes, and certain geological sources) as compared to commercial fertilizers, are used in their natural form of which they occur, and without or with minor processing (Finck 1982 in: Van Straaten 2006). Commercial fertilizers are produced by the fertilizer industry, by extracting and processing naturally occurring rocks and minerals to produce highly concentrated, soluble fertilizers (Van Straaten 2006). In the European countries, the use of easily soluble chemical fertilizers has accelerated after the Second World War (Mazoyer and Roudart 2006). The fertilizer industry focuses primarily on the three macronutrients, nitrogen (N), phosphorus (P), and potassium (K). Small amounts of secondary macronutrients and micronutrients may also be added (Yara 2015). Over time intensive farming with high yield production might lead to an impoverishment of the soil with respect to micronutrients and subsequently imbalanced nutrient status in plants (Shivay et al. 2010; Aasen 1997). Considering macronutrients and organic farming in particular, the reservoir of K and P in the soil might be depleted, even with sufficient supply of manure (Løes and Øgaard 1997). An endemic global problem is related to the nutrient leaching and runoff from agricultural land, which is a major source to eutrophication of surface waters (e.g. Withers, et al. 2014). A fertilizer that release nutrients more gradually to approach the plant´s demand in closer agreement than the mineral salts do, would be favorable (Bakken et al. 1997). In these cases, supply of crushed rocks and minerals, i.e. rock powder, helping to maintain the content of micro- and macronutrients over longer periods and remineralize the soil, is viable (Fyfe et al. 2006). Natural fertilizers that origin from minerals and rocks range from multi-nutrient silicate rock fertilizers to by-products from rock and coal processing (Van Straaten 2006). An advantage of the use of whole rock silicate fertilizers is the supply of a wide array of macro- and micronutrients in comparison to commercial fertilizers (Leonardos et al., 1987 in: Van Straaten 2006). For a rock to be accepted as a fertilizer, it is important that the plant nutrients of interest are easily available. A rock that contains biotite (K and Mg), apatite (P), carbonate (Ca, Mg) and sulfides (S) possesses favorable characteristics. Pyroxene and amphibole (Mg and Ca), and nepheline (K) are also good nutrient sources (Harley and Gilkes 2000). The aluminosilicates and ferromagnesian silicates are major rock-forming minerals that vary in structure and composition, and may be a primary source of many nutrients required for plant growth. Finely ground rock should be considered as a slow release fertilizer applied on highly depleated soils, and in leaching environments where soluble fertilizers may easily be removed (Harley and Gilkes 2000). Combined with organic nutrient sources (e.g. manure, compost), ground rock may also be used in organic farming as a viable alternative to chemical fertilizers (Harley and Gilkes 2000; Heim et al. 2012).

1.2 Carbonatite from Stjernøy, Northern-Norway

In recent years the carbonatite from the LAC, at Stjernøy, N-Norway (70° 17.75’ N, 22° 34.5’ E, Fig. 1) has been proposed as a slow-release fertilizer, because of its multifarious content of essential nutrients. Based on the classification system of natural rock fertilizers proposed by Van Straaten (2006), this rock can be classified as a multi-nutrient silicate rock fertilizer combined with liming characteristics. The main minerals are calcite (~40 wt%), biotite (~30 wt%), apatite (~7 wt%), and some nepheline (Gautneb 2009; Heim et al. 2012). Agrochemically, the high content of calcite (19% Ca) makes this rock a suitable liming material, with additional nutrient supply of K (2.6%), Mg (2.1%) and phosphorus (P, 1.3%) (Heim et al. 2012). A vegetation survey at Stjernøy (MSc Thesis by Hillersøy 2010) showed that concentrations of nutrients like Ca, K and Mg in plants were equally high or higher compared to concentrations commonly reported in northern parts of Europe (Gjengedal 2015; Reimann et al. 2001). Among the nutrients that may be supplied by silicate rock powders, K has been the most widely studied to determine whether it can become available in soils at rates significant for crop use (Harley and Gilkes, 2000). Potassium, originating from biotite and nepheline in carbonatite, was found to be recovered in harvested plants in significant amounts (Bakken et al. 1997). Of the ten rocks and minerals tested, the carbonatite gave the highest relative agronomic effectiveness (RAE = 77%), where 0% is treatment without K-fertilizer, and 100% is treatment with KCl. However, a field trial over several years, showed that carbonatite weathered too slow to replenish the indigenous pool of plant available K (Bakken et al. 2000). Carbonatite is more likely used in combination with e.g. manure or as soil amendment, rather than as an overall substitute of soluble K-fertilizer.



Figur 1: Simplified geological map of the nappes of western Finnmark (adopted and modified from Corfu et al. 2007, in Heim et al. 2012), with the Lillebukt Alkaline Complex on the island of Stjernøy located at the center of the Seiland Igneous Province (Encircled area).

1.3 Trace elements in carbonatite rock

In addition to the content of the macronutrients Ca, K, Mg, and P previously mentioned, the carbonatite contains significant amounts of micronutrients like zinc (Zn), manganese (Mn), iron (Fe), and rare earth elements (Heim et al. 2012). According to Heim (2001), there are low levels of toxic and radiogenic metals like cadmium (Cd), lead (Pb), uranium (U) and thorium (Th). However, concurrent high concentrations of barium (Ba) and strontium (Sr) are found, averaging 3200 mg kg^{-1} and 4200 in the area selected for potential exploitation of rock powder (Heim et al. 2012). Compared with the average concentrations of Ba (620 mg kg^{-1}) and Sr (310 mg kg^{-1}) in Norwegian bedrock according to the Lito-database, NGU (2010), concentrations of Ba and Sr in carbonatite from Stjernøy are classified as very high. In general, the occurrence of Ba and Sr in bedrock shows high spatial variations, and depending on the stability of minerals containing these elements, weathering will add a natural amount to the soil. In the carbonatite, Ba is primarily substituting K in the sheet interlayers of biotite, replacing up to 10% of K sites (Heim et al., 2012). Strontium on the other hand, is substituting Ca in calcite. Since both biotite and calcite are easily weathered, Ba and Sr are supposed to be released to soil in substantial amounts.

1.4 Objectives and hypotheses

The carbonatite rock from the LAC in Norway is a promising resource for exploitation as a rock fertilizer for agricultural purposes. The enrichment of Ba and Sr, however, may cause undesired uptake to plants when applied to agroecosystems. Despite that soluble Ba compounds is known to cause toxicity symptoms to plants, animals and humans (see section 2.2.3 and 2.2.4), little is known about the geochemistry and availability of naturally occurring Ba in agroecosystems. The Ba mobilization and availability from carbonatite rock powder has not been considered earlier. Knowledge on the geochemistry and bioavailability of Ba from the carbonatite rock powder is crucial in order to assess the agro-ecological risk when considering this rock to farming practices. Since Sr is supposed to have less toxicological risk in its natural occurring form, the main focus of this thesis has been on Ba.

1.4.1 General objective

The main objective of the thesis was to gain new knowledge comprising geochemistry, mobility, bioavailability and uptake of Ba to vascular plants from soils with ordinary and Ba-enriched mineralogy, with particular focus on the carbonatite rock powder.

1.4.2 Specific objectives, expectations, and hypotheses

Paper I

The primary focus of the field survey (based on the MSc Thesis work by Hillersøy (2010), was to investigate concentrations of Ba, Sr and macronutrients in vegetation growing on mineral soil developed on carbonatite and pyroxenite bedrock at Stjernøy. Availability of K, Mg, Ca, Ba, and Sr to plants was expected to be high, and closely reflect the soil mineralogy. In general, Ba and Sr were expected to be increased in plants in accordance with the acquirement for Ca.

Paper II

The effect of liming on plant uptake of Ba was investigated in a pot experiment by cultivating nine agricultural plant species in an aeolian Ba-containing sandy soil. The hypotheses, in part based on the vegetation study, were i) Under similar growing conditions, legumes concentrate more Ba than grass plants; ii) Barium follows the Ca distribution pattern within the plant, and iii) Under similar pH conditions, an increased supply of $CaCO_3$ reduces Ba uptake in plants.

Paper III

The liming effect of carbonatite compared to dolomite, and uptake of Ca, K, Mg, Ba and Sr to tall fescue and white clover grown on various sand/peat mixes was determined. The hypotheses were: i) Carbonatite is as equally as strong of a liming agent as dolomite to help buffer the pH when the organic acid content of the growth media increases; ii) There will be no difference in yield when applying equally effective liming amounts of dolomite or carbonatite to soil. Justified by the biogeochemical similarities of Ba, Sr and Ca (Marschner, 2012), we believe that: iii) Plants with a high affinity for Ca, such as legumes, will have a correspondingly high affinity for Ba and Sr, and the application of carbonatite will increase the uptake of these elements; and iv) Carbonatite application to soil will increase the geochemically labile K concentrations and create an imbalance between K-Mg-Ca in plants, compared to when only dolomite is applied.

Paper IV

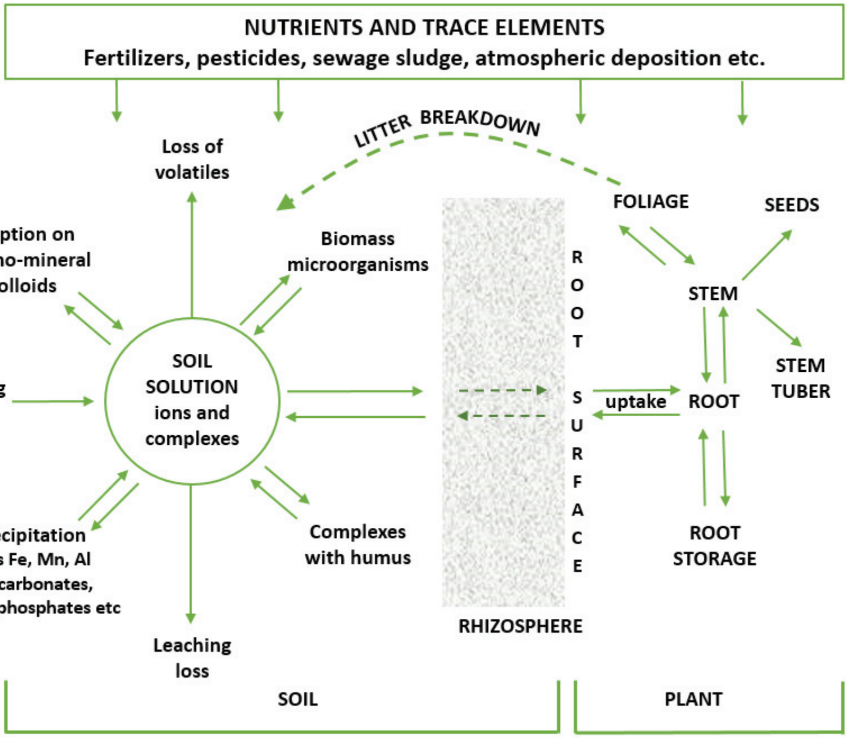
In connection with the second pot experiment (Paper III) the geochemistry of Ba in soil and pore water was investigated. The following hypotheses were addressed: (i) Ba bioavailability is controlled by the free ion activity of Ba in pore water and lability species on mineral surfaces; (ii) Ba adsorbed to dissolved fulvic substances will be mobile in soil, and therefore more available to plants; (iii) the release of Ba from carbonatite to soil will increase by supply of peat organic matter.

2 Thesis background and theoretical aspects

2.1 Nutrients and trace metals in the soil-plant system

Over time weathering of rocks under different environmental and climatic conditions leads to mobilization and transport of naturally occurring nutrients and trace metals. The soil forming processes are the same as those that determine the supply of elements to the biota in and on the soil (Fig. 2), and their altogether balance determines the nature of the soil (Anderson 1988). In the terrestrial environment, nutrients and trace metals are found within the pool of available nutrients and trace metals in the soil, in organic materials (biota and organic debris) and in soil and rock minerals (Bormann and Likens 1967, Fig. 2). Inorganic nutrients and metals taken in through the roots of plants are present in the soil solution as ions (Raven 1999; He et al. 2012). Seventeen elements are believed to be essential to all vascular plants, meaning that the elements play an important role in the plant´s metabolism, and is essential for the plants to complete their lifecycle (Raven et al. 1999; Harley and Gilkes 2000). The nine macronutrients C, H, O, N, K, Ca, Mg, P, and S are normally present in plant tissues at concentrations greater than 0.1% dry weight (DW). The eight micronutrients B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn at concentrations less than 100 $\mu g\ g^{-1}$ DW. Trace metals refer to "elements that occur in natural and perturbed environments in small amounts and that, when present in sufficient bioavailable concentrations, are toxic to living organism" (Adriano 2001). Some trace metals, like Ni, Fe and Zn, are essential at low concentrations, but toxic at high concentrations. Barium however, can be defined as a trace metal with no reported biological function (Kabata-Pendias 2011), that is considered toxic at high concentrations. In the rhizosphere solution competition between ions of the same valence (e.g. Ca^{2+}, Sr^{2+}, and Ba^{2+}) or ion diameter (Ba^{2+} and K^{+}) for entrance into plant roots is evident (Marschner 2012). Strong competition between ions does not necessarily reflect the given mineral element's role in plant metabolism, but rather the physicochemical similarities between essential and non-essential elements (Marschner 1995). Hence, the mechanisms for uptake and transport of essential nutrients from soil to plants form an entrance for non-essential and potentially toxic elements (e.g. trace metals, Cuypers et al. 2013 in: Alloway 2013). Plants form a bridge between the soil element composition and the food chain, and an important practical implication is the channeling of toxic metals into the food chain via their uptake by plants

(Marschner 1995). In the present thesis, the main focus is on the trace element Ba, and factors influencing its mobilization and availability in the soil-plant system.



Figur 2: Simplified depiction of the key components concerned with the dynamics of nutrients and trace metals in the soil-plant system (Adapted from Peterson and Alloway (1979) and slightly modified based on nutrient cycling models from Trudgill (1977), and Bormann and Likens (1967).

2.2 Barium

Barium is a dense alkaline earth metal that occur in the nature as a divalent cation in combination with other elements (Choudhury and Cary 2001). Barium is the 16th most abundant non-gaseous element of the Earth's crust, on world basis constituting 400 mg kg^{-1} in average (Choudhury and Cary, 2001; Kabata-Pendias 2011), and thereby surface waters. Barium may also be released to the environment via industrial emissions (Choudhury and Cary 2001). Barium has been identified in more than 80 minerals; however, it occurs in significant quantities only in the sparingly soluble forms of barite ($BaSO_4$) or witherite ($BaCO_3$, Boffito 1991; DiBello et al. 1991). Nearly all other Ba compounds derive mainly from raw materials of barite ore. Barium and its compounds are widely used in a number of different industrial products, like for example ceramics, cement, soap, rubber, linoleum, glass industries, electronics, roentgenography, cosmetics, inks, paints, insecticides and rodenticides, etc (Choudhury and Cary 2001).

2.2.1 Mobilization and ecosystem transfer

Barium is ubiquitous in soils, with concentrations ranging from 15 to 3500 mg kg^{-1} (ATSDR 2007). Considering the source of Ba and its influence on plant Ba uptake, the element chemical characteristics are decisive for its availability. In the nature Ba reacts easily with carbonate or sulfate ions and form insoluble salts like barite ($BaSO_4$) or witherite ($BaCO_3$) (Kabata-Pendias 2011), hence not all Ba compounds in soil are bioavailable. In soils with high cation exchange capacity (CEC), such as soils containing high contents of organic matter or clay, Ba mobility is limited by adsorption (Madejón 2013). All salts of Ba become increasingly soluble as pH decreases, with the exception of $BaSO_4$. However, mobilization of $BaSO_4$ can increase by a combination of low pH, and strongly reducing conditions (Madejón 2013). Most plants are found not to accumulate Ba, yet some do. A bioconcentration factor (Ba_{plant}/Ba_{soil}) from 2 to 20 has been reported in tomato and soybean (Choudhury and Cary 2001). Likewise, *Daruta innoxia* (toloache) has been reported to act as an accumulator of Ba (Prasad 2003). The Brazilian nut (*Bertholltia excels*) can accumulate as much as 4 g/kg (Kabata-Pendias 2011). Some few experiments, have indicated a manifold higher uptake of Ba in leguminous plant species compared to other plant groups like herbs and grasses (Robinson et al. 1950) (Madejón 2013).

2.2.2 Barium toxicity

Knowledge on the effect of Ba to physiological processes in plants are scarcely investigated (Kabata-Pendias 2011). Only a few studies have focused on plant toxicity, mostly from hydroponic cultivation using nutrient solutions and barium chloride ($BaCl_2$). The soluble forms of Ba have shown toxic effects to plants. Concentrations of about 2 g Ba kg^{-1} in trifoliate leaves of *Phaseolus vulgaris* L. (bush bean), induced toxicity by leaf withering and leaf growth inhibition, when 500 µM $BaCl_2$ were applied to a hydroponic medium (Llugany et al. 2000). This study also indicated a negative effect on Ca by Ba, and an inhibition mechanism by Ba on translocation of sulfate from roots to other plant compartments. The most Ba-sensitive parameter, however, was the K concentration in leaves, which was reduced even at concentrations that did not affect plant growth. A study by Chaudhry et al. (1977) indicated that Ba concentration in soil around 2 g kg^{-1} inhibited the growth of *Hordeum vulgare* L. (barley) and bush bean. Barium also tended to inhibit the growth of the secondary root system at certain concentrations. Suwa and co-authors (2008) found 15% yield decrease in soybean (*Glysine max* L.), in addition to an antagonistic effect of Ba on K uptake by applying 100 µM $BaCl_2$ solution to a hydroponic culture. Monteiro et al. (2011) found toxic symptoms (interveinal chlorosis followed by necrotic spots in the leaf laminae) at 225 mg kg^{-1} in leaves of Tanzanian guineagrass. Melo and colleagues (2011) reported phytotoxicity by a lowering in yield of *Glycine Max* L. (soybean) grown in an Entisol spiked with $BaCl_2$ to a concentration of 600 mg Ba kg^{-1} soil. Potentially toxic effects of Ba in plants may be reduced by adding salts containing Ca, Mg, or S, that by ion-exchange will form insoluble salts like $BaSO_4$ and $BaCO_3$ (Kabata-Pendias 2011). Yet plants may still be able to take up Ba via roots from barite contaminated soils, as indicated by e.g. Coscione and Berton (2009) and Lamb et al. (2013).

Soluble Ba-compounds are toxic to humans because Ba^{2+} has the ability to stimulate muscles and then paralyze the same muscles. A toxic dose of Ba may cause death if heart and respiratory systems are paralyzed (Pohanish, 2012). The world health organization (WHO 2004) indicated that low doses of Ba in the environment might cause unwanted effects on blood pressure. High values of Ba in the environment are hypothesized to be associated with multiple sclerosis (MS) and other nerve degenerative deceases (Purdey 2004). An important factor affecting the development of adverse health effects in humans is the solubility of the barium compound to which the individual is exposed. Soluble Ba compounds are generally expected to be of greater health concern than insoluble Ba compounds because of their greater potential for absorption (ATSDR 2007).

2.2.3 Risk assessment and critical levels

A critical level of 500 mg Ba kg^{-1} in leaves of barley has been suggested by (Davis et al. 1978), and >2000 mg Ba kg^{-1} for bush bean (Macnicol and Beckett 1985). By applying the soluble $BaCl_2$ to a hydroponic system with no addition of SO_4^{2-}, Llugany and co-workers (2000) proposed an internal lowest observed effect concentration (LOEC) for Ba at 700 and 460 mg kg^{-1} DW in primary and trifoliate leaves of bush bean, respectively.

For humans the no observed adverse effect level (NOAEL) for Ba is 0.51 mg Ba per kg bodyweight a day, and the lowest observed adverse effect level (LOAEL) is estimated to 5.1 mg Ba per kg bodyweight a day (WHO 2004). The threshold value given by USEPA for Ba in drinking water is 2.0 mg L^{-1} (USEPA 2009), and a guiding value at 0.7 mg/L is indicated by WHO (2004). In Europe, critical levels of Ba in agricultural soils have not been in focus at this point. Nonetheless, in both South- and North-America, some guidelines exist. Considering use of sewage sludge, Ba has been included in the USEPAs list comprising potential health damaging substances that need to be investigated (USEPA 2009). The Brazilian National Environment Council has established a guideline value of 300 mg Ba kg^{-1} in soils (*Brazilian National Environment Council* 2009), while in considering biosolids with agricultural potential, a maximum concentration of 1300 mg Ba kg^{-1} has been suggested (*Brazilian National Environment Council* 2006). In Canada, a quality guideline of 750 mg Ba kg^{-1} in agricultural soils has been suggested (CCME 2013). A currently approved extraction method, “Toxicity Characteristic Leaching Procedure” (TCLP, U.S. EPA Method 1311) is used to define hazardous concentrations of metals in solid wastes (e.g. landfill), where the regulatory level for Ba is set to 100 mg L^{-1} in leachates. This test can be considered an improvement to simply using the total metal content in solid materials. Nevertheless, in recent years, the method has been criticized due to the assumptions of the presence of organic matter in binding metals, and that the test does not account for other factors affecting bioavailability (Smith and Huyck, 1999). The great variation in the critical concentration of Ba in soil and soil conditioners indicates an insufficient understanding on the biogeochemistry of Ba.

2.3 Determination of mobility and ecosystem transfer of metals

Determination of the total soil content of elements is useful in many geochemical applications. The total metal concentrations in soils are often used when establishing legislation or guideline values (McGrath et al. 1994). However, the total metal content of soil include fractions that are not readily available to plants, microorganisms or soil fauna (Zhang et al. 2001). From an agricultural point of view, the biologically active fraction is of more interest to determine the availability, accessibility, mobility, or simply the extractability of elements (Cottenie et al. 1980; Bonito et al. 2008). Determination of metals in soil can be accomplished using single reagent leaching, ion exchange resins, and sequential extraction procedures (Zimmerman and Weindorf 2010). A rapid evaluation of the mobility of metals and elements in soils can be applied by speciation analyses (Jianu et al. 2012). Tack and Verloo (1995) defined speciation as "*the identification and quantification of the different, defined species, forms or phases in which an element occurs*" (Zimmerman and Weindorf 2010). Speciation of metals can help to assess how strongly they are retained in soil and how easily they may be released into soil solution (Jianu et al. 2012).

2.3.1 Single reagent extraction

There are several definitions of bioavailability (Smith and Huyck, 1999). Newman and Jagoe (1994) define bioavailability as "the degree to which a contaminant in a potential source is free for uptake (movement into or onto an organism)". Some definitions further imply that the element must affect the organism. Sposito (1989) define bioavailability as "a chemical element is bioavailable if it is present as, or can be transformed readily to, the free-ion species, if it can move to plant roots on a time scale that is relevant to plant growth and development, and if, once absorbed by the root, it affects the life cycle of the plant". In the present thesis the term bioavailability is used in the more broad sense. Several methods are developed to estimate the bioavailable fraction of nutrients and trace metals in agronomic soils (e.g. Schollenberger and Simon, 1945; Olsen et al., 1954; Egnér et al., 1960; Bray and Kurtz, 1945; Mehlich, 1984; Krogstad 1992; Jones, 1999). Common to them all is that soils are extracted with a chemical eluent, where the element concentration in the extraction solution aims to predict the potential available element fraction of soil. A chemical extractant intend to remove the entire reservoir of reactive metal, that give a total amount of metal that are several orders of magnitude higher than that found in the soil pore water (Bonito et al. 2008). In the present thesis the ammonium lactate (AL) extraction method (Egnér et al. 1960) was used in Paper I for determination of exchangeable Ba in soil, and the ammonium acetate pH 7 extraction method (Schollenberger and Simon, 1945) was used in Paper II, III and IV.

2.3.2 Diffusive gradients in thin films technique

Labile chemical species of trace metals in soils may change during sampling and extraction procedures when using conventional methods where solid and solutions are separated (e.g. disruption of pseudo-equilibrium related to the complexity of sources and sinks processes) (Hooda et al. 1999). The technique of diffusive gradients in thin films (DGT) was developed by Davidson and Zhang (1994) and has yet become an established and useful tool for the *in situ* measurements of labile metal ions in aquatic and soil environments (Zhang and Davison 2015). The DGT disk is build up in three layers: a plastic base (25 mm diameter piston) that are loaded with an ion exchange (Chelex) resin, a well-defined diffusive gel layer, and a protective membrane. The three layers are attached to the piston by a cap, leaving an open window of 20 mm at the top (Almås et al. 2006). The DGT-resin causes a depletion of metals in the close vicinity to the outside of the membrane surface, which leads to a replenishment of labile metals from the solid phase pool. Thus, the Chelex resin accumulates the labile Ba in pore water and labile Ba replenished from geochemically active binding sites in soil within the time of deployment (Hooda et al. 1999; Almås et al. 2006; Zhang et al. 1998; Zhang and Davison 2015). The DGT technique was used in Paper IV to assess the *in situ* plant available Ba fractions in soils. Due to the potential lower selectivity for Ba with time (Garmo et al. 2003), the deployment time of the DGT-resin was set to 48 hours. A detailed description of the experimental and analytical procedure comprising the DGT-analysis is described in Paper IV.

2.3.3 Chemical speciation modelling using WHAM/Model VI version 7.0.4

Chemical speciation can be determined operationally using computational software, e.g. WHAM. The software WHAM/Model VI is a chemical speciation model that determines binding site strengths of elements in soil solution (Tipping 1994; Tipping et al. 2003). The metal species are calculated based on information on cation-complexing properties of fulvic acids and humic acids, combined with sub-models determining the electrostatic effects on specific binding and counter-ion accumulation. The speciation performed in Paper IV did not account for the humic acids, only the fulvic acids. Complexation reactions with inorganic ligands in solution are also accounted for (Tipping et al. 2003). The functional relations of the metal association and dissociation to the organic acids are described in Tipping (1994, 1998). In Paper IV a detailed description of the procedure for determination of Ba^{2+} and other Ba compounds in equilibrated pore water and its associated input parameters using the WHAM speciation program is presented.

2.3.4 Transfer factor and plant distribution

The mobility and accumulation of metals in cultivated soils involve processes such as leaching, capillary forces, runoff, sorption, root uptake and re-suspension into the atmosphere. The determination of metal transfer from soil to plant can be useful to estimate the transport potential of elements from soil to plants (Tome et al. 2003). Given equilibrium conditions, transfer factors (TFs) or bio concentration factors (BCF) can be defined as the ratio of the concentrations of a trace element in plant to that of the soil (Jolly et al. 2013; Tome et al. 2003; Tagami and Uchida 2009; Chojnacka et al. 2005). Factors such as soil characteristics, climatic conditions, type of plants, tissue of the plant concerned, physico-chemical form of the element, and the effect of competitive species can influence the TF values (Bettencourt et al., 1988 in: Tome et al. 2003). Transfer factors can be evaluated when a linear relationship is observed between soil and plant composition for a given element. Such a relationship is rarely observed between the total soil content of a given metal and that of the plant. For this reason, extraction methods (see section 2.3.1) to find metal fraction that represent the available metals to plants during a growing season is necessary (Chojnacka et al. 2005). For non-essential elements like some trace metals, the linear relationship between plant concentration to that of the soil can be evident, however for essential elements that are under the strict metabolic control, the TFs does not represent linearity (Chojnacka et al. 2005). Still, the TFs may provide valuable information when comparing the ability by different types of vascular plants to acquire the given essential elements from a specific soil under similar growing conditions. In general, the exchangeable Ba measured in soil is most likely an overestimation of the actual bioavailable Ba content, since not all exchangeable Ba in the soil is readily available to plant roots. Thus, the Ba absorption potential by plants may be underestimated by the TF calculations. However, underestimation of TF is a systematic error not influencing relative comparisons of TF. The TFs or BCFs for Ba were determined in the present thesis (Paper I, II and IV).

3 Methodological approach

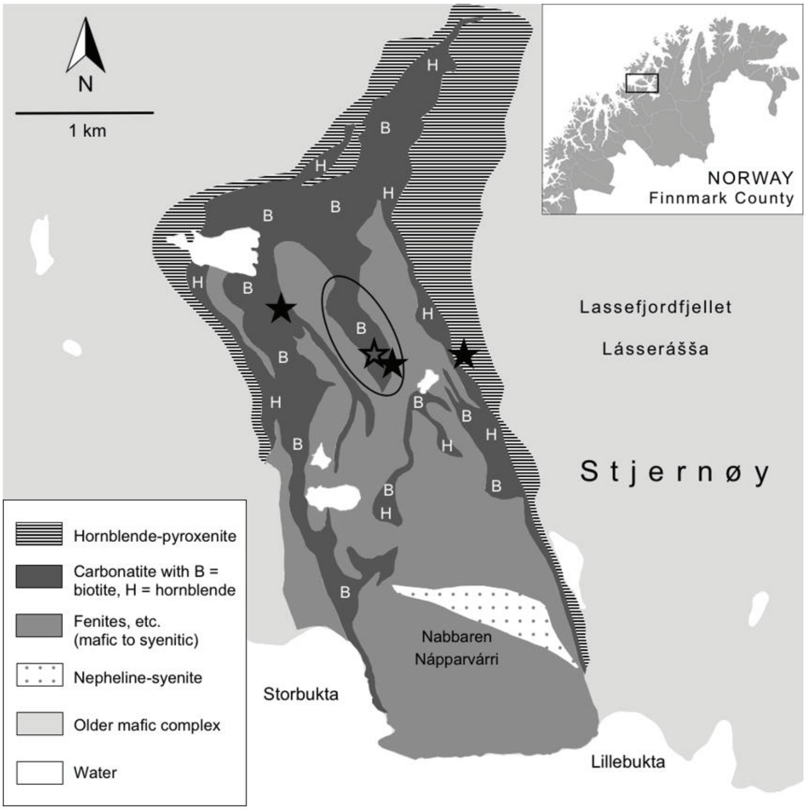
3.1 Geology of study area

The Seiland Igneous Province (SIP) covers an area of about 7000 km^2, and is a part of the Caledonian Kalak Nappe Complex, where the carbonatite was emplaced in latest Precambrian time, around 570 million years ago (Roberts et al. 2010). Mafic and ultramafic rocks dominate this magmatic province, but more differentiated types, like carbonatite and nepheline syenite are also found (Heier 1961). The carbonatite rock of agronomical interest covers about 13 km^2, and is part of the LAC, in the center of the SIP, located on the island of Stjernøy, 70^o 17.75’ N, 22^o 34.5’ E, Northern Norway (Fig. 1). The carbonatite is more precisely classified as a silico-carbonatite, due to the high contents of calcite (roughly 40 wt% $CaCO_3$) (Heim et al. 2012). A characteristic feature of the carbonatite is the separation into biotite- and calcite-rich bands (Fig. 3). As the rock is easily weathered, it is difficult to obtain representative hand specimens of the carbonatite (Heier 1961). Based on chemical analyses (XRF) of 65 samples from the central part of the carbonatite area (encircled area in Fig. 4), the carbonatite is calculated to have an average composition of about 42 wt% calcite, followed by 30 wt% biotite, and 7.5 wt% apatite. Minor constituents are nepheline, alkali-feldspar, Fe-Ti-oxides, titanite and sulphides (Heim et al. 2012). Hornblende instead of biotite is common in the peripheral carbonatite close to the hornblende pyroxenite contacts (Heier 1961, Fig. 4). In addition to carbonatite, nepheline syenite, mafic to syenitic fenites, and hornblende pyroxenite constitute the LAC (Corfu 2007, Gautneb 2009). The rich biodiversity and lushness of the flora developed on carbonatite bedrock at Stjernøy is unusual, when looking upon the high latitude (*Heier* 1961).

Figur 3: Characteristic banding by biotite and calcite in the coarse grained carbonatite bedrock at the Lillebukt alkaline complex on Stjernøy (Photo: Michael Heim).

3.2 Data sampling, experimental designs and data analysis

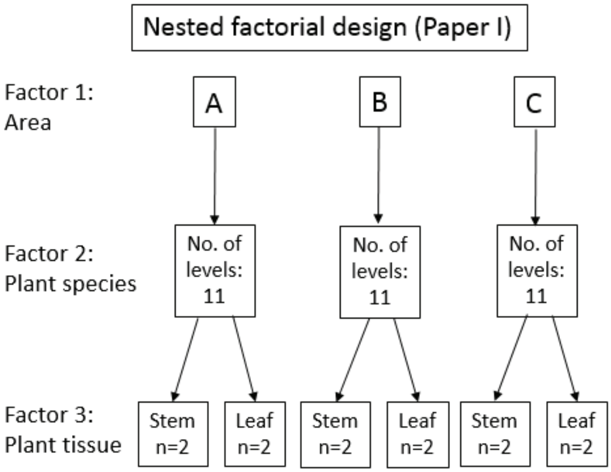
The field work at Stjernøy was carried out in August 2009, thoroughly described in the MSc Thesis Work by Hillersøy (2010), and hence, will be only briefly presented in the following chapter. The study sites located within the LAC at Stjernøy (70° 17.75' N, 22° 34.5' E) were selected based on the bedrock mineralogy. Two sites with apatite-biotite-carbonatite (short form: carbonatite) bedrock high in Ba and Sr, and one reference site with apatite-hornblende-pyroxenite bedrock lower in Ba and Sr, were chosen (Paper I). Soil and vegetation samples were collected from two comparable sub-sites of 100 to 150 m^2 within each of the three sites, represented with black stars in Fig. 4. At each sub-site, soil samples were collected in duplicates, while several plant specimen were merged into one sample. All together 29 plant species were collected, of which 23 are presented in Paper I, and 16 of these were present at all sampling sites. In the present thesis, identification and classification of all plant species were determined using Lid´s Flora (Lid and Lid, 1994). Carbonatite rock used in Paper III and IV was sampled at the location indicated by an open star in Fig. 4. With respect to the nutrient concentrations as previously described, the carbonatite within this encircled area is suitable for agricultural purposes.



Figur 4: Simplified bedrock geology of the Lillebukt alkaline complex at Stjernøy. The circle marks area for possible future mining of apatite-biotite-carbonatite rock. Black stars are sampling sites of soil and plants analysed in Paper I. Open star is sampling site for carbonatite rock used in Paper III and IV of the thesis. Illustration: Mari Haugene 2016: adapted and modified from Heim et al. (2012).

3.2.1 Field survey

In the field survey, samples of soil were collected from the soil surface to 25 cm depth using a cylindrical auger (diameter 2 cm), and stored in plastic bags at about 4°C for transportation. Field moist soil was used to determine pH_{H2O} (1:2.5 soil-water suspension, Table 2). Dried (40°C) and sieved (2 mm) soil was used to determine loss of ignition (LOI: 550°C) and ammonium lactate extracted concentrations of Ba, Sr, Mg, Ca, K and P (Egnér et al. 1960, Table 2). Plants were cut at the ground level, leaving the roots behind. Considering the dwarf shrubs, only branches were sampled. Plant samples were stored for transportation in separate paper bags and dried at 60°C for 48 hours. For most species, the dried material was divided into plant parts: stem, leaves and flower/seed. Approximately 0.250 g of accurately weighed samples of milled and sieved (2 mm) soil and plant materials were microwave digested (Milestone UltraClave 3) at 250°C with nitric acid (65 wt% HNO_3, sub-boiled ultrapure). Concentrations of Ba, Sr, Ca, K, Mg, P, and S were determined using inductive coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Siex Elan 6000) and inductive coupled plasma optical emission spectrometry (ICP-OES (Perkin Elmer Optima 5300DV). In Paper I, the Ba concentrations in leaves of 16 plant species represented at all three sampling areas were compared using a factorial design (Fig. 5). The grouped level predictor allow for testing the main effects only, and not interactions (Schielzeth and Nakagawa 2013).

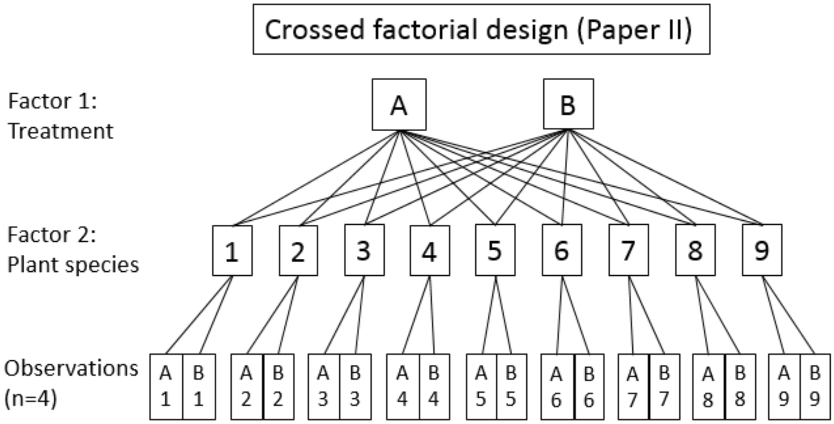


Figur 5: Simplified depiction of the experimental design used in Paper I. Note that each of the eleven levels (Factor 2) represent individual plant species, that each are given 2 sublevels (Factor 3).

3.2.2 Pot experiments

Based on findings of Paper I a pot experiment was carried out autumn 2012 and spring 2013. Nine plant species of grasses, tuber vegetables and herbs, including *Vicia cracca* (bird vetch), were grown in an aeolian sand dominated by the tectosilicates quartz and feldspars (1.3% clay/silt, 98% sand, d_{50} = 0.4 mm) supplied with 1.3 wt% peat. The sand originates from

Starmoen, east of Elverum, Norway, where wind-blown sediments of fluvioglacial material were emplaced after the last ice age (Klemsdal 2010). This sand is commonly used as model soil in pot experiments at the Norwegian University of Life Sciences, due to its composition of well sorted, fine grained minerals (Appendix II), low CEC and low buffering capacity. Using non-perforated 3 dm^3 pots, each plant species were given four replicates supplied with a control (A = 100 mL 0.075 M NaOH) and four replicates supplied with lime treatment (B = $CaCO_3$, Fig. 6). Shoots of all the species including roots of five of these, were harvested at maturity of flowering. The soil was analyzed for pH, exchangeable Ba (ammonium acetate pH 7.0, Schollenberger and Simon, 1945, Table 2), cation exchange capacity (CEC), base saturation (BS), and total organic carbon (TOC, TruSpec analyzer, Nelson and Sommers, 1982). Total Ba concentration in the sand was determined by x-ray fluorescence (XRF) analysis (www.acmelabs.com). Ammonium acetate extracted Ba in soil, nitric acid and hydrofluoric acid extracted concentrations of Ba in soil, and nitric acid extractable Ba concentrations of plant samples (Table 2, Appendix I) were determined by ICP-MS (Agilent 8800 Triple Quadrupole). For details on the methodological approach and experimental setup, see Paper II. A simplified depiction of the factorial design used is provided in Fig. 6. The crossed model selection was applied to address potential interactions among factors and levels (Montgomery 2009) on the response in Ba uptake to plants.



Figur 6: Experimental design used in the first pot experiment (Paper II). Group levels (individual plant species) are labelled with numbers, and treatment levels (A= control without $CaCO_3$, B = pots supplied with $CaCO_3$) are labelled by upper-case letters.

Based on findings of Paper I and II, one grass species (*Festuca arundinácea*, tall fescue) with low potential for Ba and Ca uptake, and one legume (*Trifolium repens*, white clover) with higher potential for Ba and Ca uptake was selected for a second pot experiment (Paper III and IV), that was carried out in autumn 2013 and spring 2014. The same type of sand as previously described was used as the basic growth medium, and mixed with different vol% peat in 3 dm^3 non-perforated pots. Pots were supplied with macro- and micronutrients (Appendix III), and treated with liming agents either as dolomite or carbonatite. Plant were grown under controlled conditions in a greenhouse, and shoots were harvested at 6, 10 and 14 weeks. Using the same analytical procedure as for Paper II, the growth media were analyzed for exchangeable Ba (Table 2), CEC and TOC. Data for carbonatite grain size is presented in Appendix II. Nitric acid and hydrofluoric acid extracted concentrations of Ba, Sr, Ca, Mg and K in soil and nitric acid extractable concentrations (Table 2) of the same elements in plant samples were determined using ICP-MS (Agilent 8800 Triple Quadrupole). A detailed description of the experimental setup is provided in Paper III and IV. In Paper III a factorial design (Montgomery 2009) was used to address the Ba uptake by plants as affected by different treatments (Table 1).

Table 1: Crossed factorial design in the second pot experiment (Paper III).

Design factors				Barium uptake by plants (replicates)			
Peat vol%	Treatment	Plant species	Harvest (weeks)	1	2	3	4
5	Dolomite	Tall fescue	6, 10, 14	-	-	-	-
20	Dolomite	Tall fescue	6, 10, 14	-	-	-	-
50	Dolomite	Tall fescue	6, 10, 14	-	-	-	-
5	Carbonatite	Tall fescue	6, 10, 14	-	-	-	-
20	Carbonatite	Tall fescue	6, 10, 14	-	-	-	-
50	Carbonatite	Tall fescue	6, 10, 14	-	-	-	-
5	Dolomite	White clover	6, 10, 14	-	-	-	-
20	Dolomite	White clover	6, 10, 14	-	-	-	-
50	Dolomite	White clover	6, 10, 14	-	-	-	-
5	Carbonatite	White clover	6, 10, 14	-	-	-	-
20	Carbonatite	White clover	6, 10, 14	-	-	-	-
50	Carbonatite	White clover	6, 10, 14	-	-	-	-

As part of the second pot experiment, Ba speciation in soil and pore water was performed (Paper IV). One week before the first harvest, DGT samplers were carefully inserted into the top soil, one for each treatment combination (Fig. 7). To test replicate variability one set of DGT disks were deployed into each pot replicate (4 replicates) of one treatment combination. After 48 h the DGT resins were removed and rinsed with deionized water before dismantling. Pore water was collected from separate bulk samples of "undisturbed" soil (i.e. not influences by rhizosphere activity) from each soil treatment combination provided in the second pot experiment (n=12). Concentrations of Ba in the DGT disks, and Ba, Sr, Ca, Mg, K, Na, Fe, S and Al in pore water were determined by ICP-MS (Table 2). Dissolved organic carbon (DOC) was determined by Shimadzu TOC-5000 analyzer. Speciation of Ba in pore water was calculated using WHAM/Model VI version 7.0.4 for waters. A detailed description of the experimental setup related to the geochemistry of Ba in soil and pore water is provided in Paper IV.

Figur 7: Second pot experiment (Paper III and IV) autumn 2013 showing the two plant species *Trifolium repens* L. (tall fescue) and *Festuca arundinácea* L. (white clover). For each treatment combination n=4. Inset: DGT-sampler embedded into soil one week before the first harvest.

Table 2: Overview of the extraction methods and analyses used in the thesis.

Method	Description	Purpose	Analysis
Acid digestion	Min. 65 wt% HNO_3 and/or 48 wt% HF and H_2O (ratio 5:1:2) with 0.2 g sample and 6 mL acid. Closed microwave digestion (250ºC hold time 20 min.).	Total concentration of elements in soil materials (Paper I-IV).	ICP-MS and ICP-OES.
Acid digestion	65 wt% HNO_3 and H_2O (ratio 5:2) with 0.2 g sample and 5 mL acid.	Total content of elements in plant samples (Paper I-IV).	ICP-MS and ICP-OES.
Ammonium lactate extraction	Method based on Egnér et al. (1960).	Exchangeable Ba in soil (Paper I).	ICP-MS and ICP-OES.
Ammonium acetate pH 7 method	Method based on Schollenberger and Simon (1945).	Exchangeable Ba in soil (Paper II, III, IV).	ICP-MS.
Pore water extraction	Equilibrated pore water vacuum collected and filtered through 45 µm membrane filters. and conserved with 0.5 mL EDTA before element analysis. Samples for TOC determination were not conserved with EDTA.	Pore water sampling in growth media for determination of base cations, Ba, DOC (Paper IV).	ICP-MS, Shimadzu TOC-5000 analyzer.
Diffusive gradients in thin films technique (DGT)	Emplaced *in situ* of top soil for 48 h deployment time. Resins eluted with min. 65 wt% HNO_3. Eluates diluted with de-ionized water prior to analysis.	*In situ* exchangeable Ba in soil-pore water interface (Paper IV).	ICP-MS.
pH-determination	10 mL soil samples mixed with 2.5 mL de-ionized water, shaken and equilibrated for minimum 24 h. Then shaken and sedimented for 1 h prior to pH-determination.	Characteristics of soil: acidity (Paper I-IV).	pH-meter: combined glass membrane electrode.

3.3 Data analysis and statistics

3.3.1 Used parameters and equations

The phytoextraction potential (bio concentration) of Ba by plants (Eq. 1), the process leading to higher plant tissue concentrations of Ba than the exchangeable Ba concentration in soil, was calculated using the bio concentration factor (BCF, Paper II), or the transfer factor (TF, Paper I and IV).

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$$\mathrm{TF} = \frac{[\text{Plant Ba (DW)}]}{[\text{Soil Ba}_{\text{exc}}\text{ (DW)}]} \qquad [1],$$

where *[Plant Ba (DW)]* is the concentration of Ba in dry weight (DW) plant samples, and *[Soil Ba$_{exc}$]* is the concentration of exchangeable Ba in soil.

By taking into account the differences in yield dry weight (DW) of the different plant species the total Ba uptake was calculated in Paper II, III and IV (Eq. 2):

$$\text{Plant Ba (mg pot}^{-1}\text{)} = \frac{[\text{Plant Ba}]\ (\frac{\text{mg}}{\text{kg}})}{1000\ \left(\frac{\text{g}}{\text{kg}}\right)} \text{ x DW (g pot}^{-1}\text{)} \qquad [2],$$

Translocation of Ba from roots to shoots (Eq. 3, Paper II) was calculated using the translocation index (TI).

$$\mathrm{TI} = \frac{\text{Ba shoots DW} \left(\frac{mg}{pot}\right)}{\text{Ba whole plant DW} \left(\frac{mg}{pot}\right)} \qquad [3],$$

where *Ba shoots DW* is the total uptake of Ba in shoot tissue (above ground plant parts) of the plants (mg pot^{-1}), and *Ba whole plant DW* is the total plant uptake of Ba in both shoots and roots (mg pot^{-1}).

In Paper IV, concentrations of Ba in the DGT-resins were given in µg L^{-1} by the ICP-MS. The true Ba concentration in the DGT-samplers were determined based on Eq. 4a and 4b.

The mass of metal in the resin gel (M) was obtained using Eq. 4a.

$$M = Ce\,\left(\frac{VHNO_3 + Vgel}{fe}\right) \qquad [4a],$$

where *Ce* is the concentration of metals in the 1M HNO_3 elution solution (in µg/L), *$VHNO_3$* is the volume of HNO_3 added to the resin gel (10 mL), *Vgel* is the volume of the resin gel (0.15 mL), and *fe* is the elution factor for each metal (0.8).

Then, the concentration of metal measured by DGT was calculated using Eq. 4b.

$$[DGT] = \frac{M\Delta g}{DtA} \qquad [4b],$$

where Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.13 mm), D is the diffusion coefficient of metal in the gel ($4.2 \cdot 10^{-6}$), t is deployment time (48 h) and A is the exposure area ($A = 3.14\ cm^2$).

3.3.2 Statistical analysis

In this thesis univariate statistics (arithmetic and geometric mean values, ANOVA, correlation and regression analyses, pair-wise and two sample t-tests) were calculated using the software programs Microsoft Excel (2007) and R ($R_{x64\ 3.2.2}$ and $R_{commander}$; Faraway 2002). Non-parametric tests (Paper I) were performed using the XLstat software for Microsoft Excel (2007). In addition multivariate statistics (principal component analysis, Paper III) and multiple regression analysis), ANOVA, and Tukey's familywise test were performed using the software JMP Pro 12 (SAS Institute Inc. 2013), and $R_{commander}$, in order to involve multiple testing of variables, and their interaction. For all the statistical analyses significance was determined within 95% confidence limits ($\alpha = 0.05$), meaning of $p < 0.05$. The data analyzed were checked for normal distribution (normal quantile plots) and homogeneity of variance (residual vs fitted plots). In cases for which data were not normally distributed, lognormal transformation was performed.

4 Summary of the scientific papers

4.1 PAPER I – Uptake of macro nutrients, barium and strontium to vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway

Carbonatite originating from the Lillebukt Alkaline Complex at Stjernøy in Northern Norway possesses favorable lime and potassium (K) fertilizer characteristics. However, enrichments of barium (Ba) and strontium (Sr) in carbonatite may cause an undesired uptake by plants when applied to agroecosystems. A field survey was carried out to compare concentrations of Ba, Sr, and macronutrients in indigenous plants growing in mineral soil developed on a bedrock of apatite-biotite-carbonatite (high in Ba and Sr) and of apatite-hornblende-pyroxenite (low in Ba and Sr) at Stjernøy. Samples of soil and vegetation were collected from three sites, two on carbonatite bedrock and one on pyroxenite bedrock. Ammonium lactate (AL)-extracted soil samples and nitric acid microwave-digested samples of soil, grasses, dwarf shrubs, and herbs were analyzed for element concentration using ICP-MS and ICP-OES. Concentrations of magnesium (Mg) and calcium (Ca) in both soil (AL) and plants were equal to or higher compared to values commonly reported. A high transfer of phosphorus (P) from soil to plants indicates that the apatite-P is available to plants, particularly in pyroxenite soil. The non-exchangeable K reservoir in the soil made a significant contribution to the elevated K transfer from soil to plant. Total concentrations of Ba and Sr in surface soil exhibited a high spatial variation ranging from 490 to 5300 mg Ba kg^{-1} and from 320 to 1300 mg Sr kg^{-1}. The transfer of AL-extractable elements from soil to plants increased in the order Ba < Sr < Ca < Mg < K, hence reflecting the chemical binding strength of these elements. Concentrations of Ba and Sr were low in grasses (~20 mg kg^{-1}), intermediate in dwarf shrubs and highest in herbs. Plant species and their affinity for Ca seemed more important in explaining the uptake of Ba and Sr than the soil concentration of these elements. The leguminous plant species *Vicia cracca* acted as an accumulator of both Ba (1800 mg kg^{-1}) and Sr (2300 mg kg^{-1}).

4.2 PAPER II - Can liming reduce barium uptake by agricultural plants grown on sandy soil?

This study investigated the treatment effect of lime ($CaCO_3$) added to a sandy soil containing a total of 500 mg Ba kg^{-1} on uptake and interspecies distribution of Ba in legumes and other cultivated food and feed plants. Nine species of grass, vegetables, herbs, and legumes were cultivated under controlled conditions in a greenhouse experiment. The plants were harvested at maturity or flowering, dried, milled, and digested with nitric acid using the microwave technique prior to analysis by ICP-MS. All plant species extracted Ba from the soil in considerable amounts, probably due to low Ba adsorption potential in the sandy soil. Shoot tissue concentrations ranged from about 100 (grass) to 600 mg Ba kg^{-1} (legumes), and root concentrations from about 100 (tuber vegetables) to 700 mg kg^{-1} (legume). *Vicia cracca* L. (bird vetch) showed accumulation capacity due to high shoot concentrations of Ba compared with the other species. Higher yield accompanied by a potential dilution effect can partly explain why *Trifolium repens* L. (white clover), *Pisum sativum* ssp. *arvénse* L. (gray pea) and *Hordeum vulgare* L. (barley) did not display the highest Ba concentrations, but showed the highest Ba uptake from soil. High plant uptake of calcium (Ca) also seemed to enhance Ba uptake, by legumes in particular. However, liming reduced shoot Ba concentrations, particularly in species with low affinity for Ca, but not in species with higher affinity for Ca, like *V. cracca*. The risk of Ba accumulation thus raises toxicity concerns when forage legumes are cultivated in soils containing elevated concentrations of Ba.

4.3 PAPER III – Use of carbonatite rock as fertilizer and liming agent, and uptake of Ba, Sr, Ca, Mg and K to *Fesctuca arundinácea* and *Trifolium repens* on increasing the supply of peat

Carbonatite rock powder originating from the Lillebukt Alkaline Complex at Stjernøy in northern Norway can potentially be used as a slow-releasing lime and potassium (K) fertilizer, due to a high content of the easily weathered minerals calcite (42 wt%) and biotite (30 wt%). However, the enrichment of barium (3 g Ba kg^{-1}) and strontium (4 g Sr kg^{-1}) may cause an undesired uptake to plants when carbonatite is applied to agroecosystems. A pot experiment was designed to investigate the liming and K-fertilization effect of carbonatite and the potential mobilization of Ba and Sr compared to a dolomite lime commonly used in Norwegian agriculture. These liming agents were mixed with a sandy soil applied to different amounts of peat, and the uptake of Ba, Sr, calcium (Ca), magnesium (Mg) and K uptake in

Festuca arundinácea Schreb. (tall fescue) and *Trifolium repens* L. (white clover) were evaluated. The liming agents were generally incapable of buffering the acidifying effect from increased applications of peat, while the plant dry mass was unaffected. Compared to pots given dolomite and soluble K, the availability of K from carbonatite to plants was equally high or higher, and no difference in the K/(Ca+Mg) ratio in plants was observed. Carbonatite was a significant source to plant Ba and Sr, and the uptake seemed to follow the Ca uptake. Addition of peat amplified the uptake of Ba, Sr, Ca, Mg and K to plants, probably an effect of organic acid-induced weathering of carbonatite. White clover took up Ba, Sr and Ca more effectively than tall fescue, but the Ba and Sr concentrations in plants were relatively moderate compared to concentrations reported from field investigations. The pot experiment should be accompanied by field trials to investigate the impact of climatic conditions, leaching and runoff on the nutrient balance when carbonatite is used as a soil conditioner.

4.4 PAPER IV – Geochemistry of barium in soils supplied with carbonatite rock powder and barium uptake to plants

Apatite-biotite-carbonatite (short form: carbonatite) rock powder originating from Lillebukt alkaline complex, N-Norway is a potential liming and multi-nutrient fertilizer. However, the elevated contents of potentially bio-toxic barium (Ba) (up to 5.5 g kg^{-1}) is a matter of concern. A pot experiment was conducted in order to investigate the geochemistry of Ba in a sandy peat-containing growth media treated with carbonatite, with special focus on Ba-speciation in the pore water. These results were correlated with Ba uptake in *Trifolium repens* L. (white clover) and *Fesctua arundinácea* L. (tall fescue). The Ba-speciation and bioavailability as affected by treatment and plant growth was conducted using WHAM/Model VI version 7.0.4 and the diffusive gradients in thin films (DGT) technique, respectively. The increasing cation exchange capacity (CEC) in the growth media, and colloidal fulvic acids (FA) decreased the Ba^{2+} concentration in pore water. Both the Ba detected in DGT (Ba_{dgt}), and exchangeable Ba (Ba_{exc}) were higher in pots containing rock powder. A strong relationship between Ba_{exc} and diffusively bound Ba to FA (Ba_{dfa}) with plant uptake was evident. The latter was likely initiated by organic material mobilization of Ba from carbonatite. The mobilised Ba bound to FA (Ba_{fa}) in pore water was mainly bound diffusively, and the Ba_{dfa} fraction was thus made available to plants. Finally, the Ba_{dgt} was increased in pots grown with white clover compared to tall fescue. Further investigation is required to determine if this is related to increased rhizosphere activity by plants or to the nitrogen fixating plant-microbe relationship.

5 Main results and discussion

5.1 Chemical analysis and data quality

To ensure good data quality the necessary effort and care were made during the planning of the experiments, throughout the experimental period, and at sampling, storage and measurements. Soil samples were carefully mixed in order to obtain the most representative sampling for element determination. Soil and plant samples were dried immediately after harvest in order to prevent decomposition. Dried samples were stored in a dry and dark environment until chemical analysis. All the equipment used throughout were clean, and the reagents were of pro-analysis quality. Furthermore, method performance was monitored with concurrent analysis of blanks, quality control samples made of certified standard solutions, and certified reference materials (CRM) of soils and plant matrices. Examples of accuracy control are presented in Table 3. The CRM for exchangeable Ba in soils were in accordance with the certified values issued. For acid extracted mineral soils in general, the recovery was lower than expected, but mostly within 3 times standard deviation of the certified value. Nevertheless, the XRF-analyses gave a better estimate of total element concentration in mineral soils, compared to the acid extractable concentration. A within-laboratory precision test, performed on 8 parallel samples of the eolean sand, and 6 parallel samples of carbonatite that were acid digested and analyzed by ICP-MS in the same way as other soil samples, had a relative standard deviation (% RSD) of 4% and 16% for Ba, respectively. According to Essington (2004), RSD values below 15% indicate little variability in a dataset, while RSD between 16 and 35% indicate moderate variability, and RSD above 36% indicate high variability, and a relatively heterogeneous dataset. Hence, the composition of the aeolian sand can be classified as relatively homogeneous, while the carbonatite rock powder is moderately heterogeneous. Brown (1998) suggest that RSD values below 30% can be considered as a good or fairly good precision in a dataset. In general, plant samples analyzed in the pot experiments had RSD (n=4) below 30%. Thus, measurements of element concentrations were obtained with acceptable accuracy and precision. Details of how the procedures were conducted and their corresponding interpretations are provided later in the scientific papers (Paper I-V).

Table 3: Acid extracted concentrations of selected elements (mg kg^{-1}) measured in standard reference materials (SRM, plant material). Values are in accordance with the certified or indicated values issued, if nothing else is noted.

			Ba	Sr	Ca	Mg	K	P	S
Paper I ICP-OES	IAEA-V-10 Hay	n=11	5.3±0.2	41±0.7	21300±360	1340±21	21300±471	2300±50	2800±150^{c}
	CNACIS 2004c Leaves of Poplar	n=11	27.2±0.8	154±2.5	17700±400	6380±66	13900±220	1630±30	3300±170
	CNACIS 2004b Bush Branch	n=11	19±0.6	342±8	22200±400	2860±51	8400±250	850±20	3200±130
Paper II	NCS DC 73348 Bush twigs & leaves	n=6	18±0.5	335±8.4	21400±360	2770±52	7700±190	790±17	3300±170
ICP-MS	IAEA-V-10 Hay	n=6	5.0±0.1	38±1.8	19500±650	1280±41	20200±1170	2200±0	2900±150^{c}
	GBW 07603 Bush branch & leaves	n=2	19^{a}	230^{a}	16000^{a}	4600^{a}	9600^{a}	990^{a}	695^{a}
	NCS ZC73013 Spinach	n=1	9.7	75^{b}	5700^{b}	5100^{b}	24000	3400	4400
Paper III and IV	IAEA-V-10 Hay	n=1	5.2	39	19000^{b}	1300	21000	2400	2800^{c}
ICP MS	1515 Apple leaves NIST	n=1	48^{a}	23^{a}	14000^{a}	2700^{a}	16000^{a}	1600^{a}	1800^{a}
	1575 Pine needles NIST	n=1	7.3	4.7	4300	1200	3900	1200^{b}	1200^{c}
	1570a Spinach	n=1	7.4^{c}	52^{b}	15000	8700^{c}	28000^{b}	5500^{b}	4800

[a] Value is given as an indicated value without uncertainty in the certificate.

[b] Value not within certified area.

[c] no value is given in the certificate.

5.2 Geochemistry of the Ba sources

The sources of Ba investigated in this thesis originate from natural minerals, mainly feldspars (XRF: 500 mg Ba kg^{-1}), carbonatite (bedrock, XRF: 3 200 mg Ba kg^{-1}) and pyroxenite (bedrock, XRF: 760 mg Ba kg^{-1}). The carbonatite soil at Stjernøy (Paper I) contained Ba concentrations above the agricultural soil quality limits of 750 mg kg^{-1} suggested by the Canadian soil quality guidelines (CCME, 2013), and the maximum concentration of 1300 mg Ba kg^{-1} in biosolids with agricultural potential suggested by the *Brazilian national environment council* 2006). The area for potential exploitation of carbonatite at Stjernøy contains Ba in concentrations above values reported to induce significant yield reduction of bush bean (Chaudhry et al., 1977). In principle, the carbonatite rock could be classified as a potential hazardous material. However, as briefly described in chapter 2.3, the total Ba concentration of soil include fractions that are not readily available to plants. The plant available fraction of Ba depends on soil chemistry and is lower than the total concentration. The AL-extractable (Paper I) or ammonium lactate-extractable (Paper II-IV) element concentration could be a closer approach to determine exchangeability of elements in soils, which in turn reflects the availability to plants (e.g. Øgaard et al., 2002). In the area of potential exploitation of carbonatite at Stjernøy, the AL-soluble content of Ba was 230 mg kg^{-1} in average (Paper I), about nine times higher than average AL-soluble Ba in soils of northern part of Europe and Russia reported by Reimann (2001). However, little is known about the biologically active fraction of Ba in soil that can be considered critical, making risk assessment for the use of carbonatite rock challenging.

The aeolian sand used in Paper II-IV is mainly composited of tectosilicates, i.e. quartz and feldspars, where Ba mainly originates from K-feldspar and some from plagioklas (Heier 1962). For tectosilicates in general, Al^{3+} has isomorphically substituted some of the Si^{4+}, which in turn requires monovalent cations (Na^+ or K^+) for charge balance (Essington 2004). In turn, Ba^{2+} can isomorphically substitute for K^+ due to similar ionic radius (Heier 1962). These elements are probably specifically bound in the mineral lattice of silica, and thus, highly resistant to weathering or degradation (Bakken et al., 1997). The mineral nutrition to plants by this sand is insufficient, despite high total concentration of e.g. K (see Table 1, Paper III). Compared to soluble Ba sources, the aeolian sand was assumed to give a more realistic prediction of Ba uptake, as the Ba taken up by plants would originate from feldspar particles, representing about 30% of the sand. Barium in the sand was expected to be bound primarily to non-exchangeable sites on feldspars; however, as seen in Paper II-IV a considerable fraction was indeed exchangeable. In carbonatite, Ba originates mainly from the biotite fraction, were Ba replaces up to 10% of the K sites in the sheet interlayers (Heim et al. 2012). Biotite is a relatively easily weathered mineral; accordingly, Ba might be mobilized in soils where carbonatite is present in considerable amounts. Considering the source of K, the nutrient release from biotite is found to be relatively high, while K from feldspars is nearly unavailable (Gautneb and Bakken, 1995, Bakken et al. 1997, 2000). Biotite serves as the primary source of available K in the applied carbonatite rock powder in this thesis. As biotite bound K is taken up by plants in significant amounts, reaching the levels comparable with soluble K fertilizer (Bakken et al. 1997), a significant availability of Ba is also suggested due to similar geochemistry of these elements (Kabata-Pendias 2011). This was also demonstrated by an increased exchangeable Ba content in soils supplied with ABC rock powder in Paper III/IV. As the pyroxenite soil of Paper I contains very little biotite, Ba can be expected to derive from the pyroxene or the hornblende fraction. Other sources of Ba are related to the dolomite and peat (Paper II – IV), where the Ba concentrations were considered negligible compared to the Ba from sand and carbonatite, and will not be further discussed.

5.3 Mobilization of Ba from mineral soil

The Ba speciation in soil and pore water (PW) of Paper IV showed that the most significant factors controlling immobilization of free Ba^{2+} (log-normalized) in PW was the cation exchange capacity (CEC, $r^2 = 0.97$, $n = 12$, $p < 0.001$, Fig. 8b), which in turn was closely related to the total organic carbon (TOC) content derived from peat. As the fraction of Ba in PW bound to colloidal fulvic acids (FA) increased, the Ba^{2+} concentration decreased ($r^2 = 0.85$, $n = 12$, $p < 0.001$, Fig. 8a). The significance of soil organic matter (SOM) in binding Ba^{2+} agrees with findings in literature, reporting increased sorption of Ba in soils with high CEC (Madejón 2010). In the present thesis, cation exchange capacity is mostly controlled by SOM, and Lee and co-workers (2007) reported that muscovite, particularly when coated with SOM, showed great sorption capacity for Ba. Although Ba is easily adsorbed by SOM, as well as by oxides and hydroxides, it can be relatively mobile in soils, particularly in acid ones (Kabata-Pendias 2011). This is probably because Ba primarily binds to soil particles by ion exchange (Menzie et al. 2008; Zhang et al. 2001), and, although Ba is known to have high affinity for SOM, such complexes are not very strong (Smith et al. 2004). Electrostatic forces account for a large fraction of the non-specific sorption of Ba on soil and subsoil, and the retention of Ba, like that of other alkaline earth cations, is largely controlled by the CEC of the sorbent (Choudhury and Cary 2001). Leaching experiments indicate that the formation of soluble organic Ba complexes from domestic wastes can contribute to Ba mobility in soils (Lagas et al. 1984). In situations where SOM is adsorbed to biotite from e.g. carbonatite, weathered Ba from biotite will most likely be transferred to SOM, which in turn can be mobilized to pore water as Ba-DOM colloids.

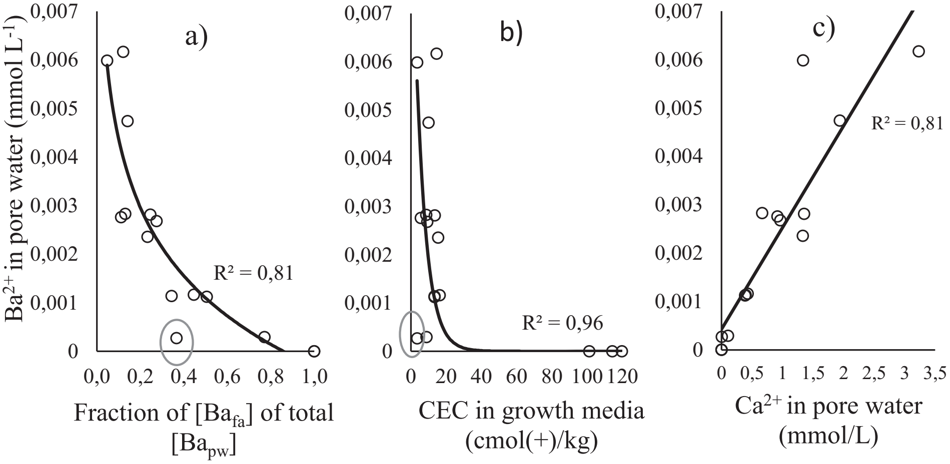
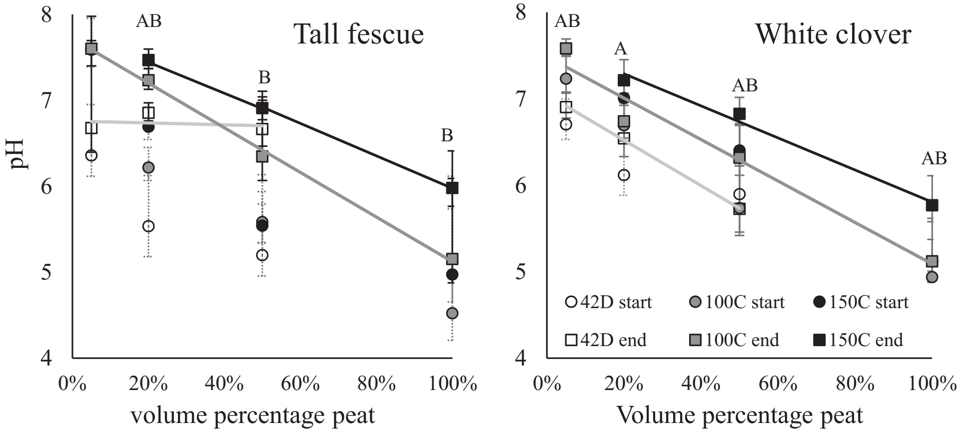


Figure 8: Ba^{2+} concentration in pore water related to a) the fraction of Ba bound to colloidal fulvic acids in pore water (Ba_{fa}/Ba_{pw}), b) cation exchange capacity (CEC) of growth media, and c) Ca^{2+} concentration in pore water. The encircled points mark the sandy soil (control) without lime or carbonatite rock powder.

In general, the soil liming effect of carbonatite is effective when weathering and dissolution of its associated minerals takes place (Paper III). The latter is possibly affected by the presence of organic acids derived from peat, that alter the weathering of silicate minerals (e.g. Essington, 2004), and such increases the solubility of Ba salts (Madejón, 2013). Besides the fall in pH as the vol% of supplied peat increase, peat derived organic acids seems to have mobilised Ba, and thus increased the availability to plants (Paper III and IV). The biogeochemical processes can indirectly be measured as changes in pH over time, and in Paper III, the pH generally increased from start towards termination of the pot experiment within each treatment combinations (Fig. 9). That is interpreted as an indication of carbonatite and dolomite weathering during the trial period. Compared to tall fescue treated with dolomite, a stronger reduction of pH in the dolomite treated pots of white clover indicate stronger active uptake regime, in one way or the other, and probably also higher biological activity in the rhizosphere.



Figur 8a and b: Mean pH ±SD in pots of tall fescue and white clover at the start and at the end of the pot experiment. The trend lines are connecting equal mineral treatments with pH observations at the end of the experiment. 42D = 42 dolomite pot^{-1}. 100C and 150C = 100 and 150 g carbonatite pot^{-1}. A significant difference in pH ($p<0.05$) resulting from carbonatite treatment compared to the apparent equal liming effect caused by dolomite within each growth media is indicated with the upper-case letter A. A significant increase in pH ($p<0.05$) within each treatment and growth media from start to end of the pot experiment is indicated by upper-case letter B on the top of the end-pH columns. Statistics are performed by two sample t-test (95% confidence level, CL).

Uptake of mineral nutrients and excretion of protons at the root surface are, in addition to microbial activity, processes that amplifies the weathering of minerals in the rhizosphere (Rengel and Marschner 2005; Dotaniya and Meena 2015). The Ba_{dgt} measurements (Paper IV) showed substantially higher concentrations of Ba_{dgt} in soil grown with white clover (ranging from 1 to 11 µg L^{-1}, with a median of 7.8) compared to soils grown with tall fescue (ranging from 1 to 6 µg L^{-1}, with a median of 3). The increased Ba_{dgt} in soil of white clover supports the indication of an active plant factor in the rhizosphere, mobilizing mineral bound Ba from soil. The experiment was not designed to test possible microbial impact at the rhizosphere, hence it is unclear whether the increased Ba_{dgt} in the rhizosphere of white clover is connected to an increased microbial activity (Coscione and Berton 2009), or whether this is simply connected to the properties of white clover as a dicot plant.

5.4 Barium uptake to plants

In general, concentrations of Ba in vegetation grown on carbonatite or pyroxenite soil at Stjernøy (Paper I) were in accordance with or higher compared with Ba concentrations in plants observed in northern parts of Europe (Reimann et al., 2001; Gjengedal et al., 2015). In general, median tissue concentrations and transfer factor ranges (TFs) of Ba were lowest in grasses (30 mg kg^{-1}, TF: 0.06 – 2.1), intermediate in dwarf shrubs (100 mg kg^{-1}, TF: 0.4 - 8) and higher in herbs (150 mg kg^{-1}, TF: 0.4 -17). Very high tissue concentrations were observed in the leguminous species *Vicia cracca* L. (bird vetch), on average 2 g kg^{-1}. In the first pot experiment (Paper II), lowest concentrations and TFs were observed in shoots of the grass species *Festuca arundinácea* L. (110 mg kg^{-1}, TF: 6), and highest in the legumes *Trifolium repens* L. (500 mg kg^{-1}, TF: 22) and bird vetch (600 mg kg^{-1}, TF: 25). In the second pot experiment average Ba concentrations ranged from 13 to 50 mg kg^{-1} in tall fescue (TF: 0.9 – 2), and 18 to 90 mg kg^{-1} in white clover (TF: 0.8 – 3). Variations in plant Ba contents in this thesis confirm the importance of considering factors controlling Ba availability such as soil properties, Ba source, growth conditions, and plant induced mobilization of elements.

5.4.1 Availability of Ba to plants

The Ba uptake to plants observed in Paper II, and in dolomite treated pots of Paper III/IV is suggested to derive mainly from the sparingly soluble feldspar fraction of the sandy soil. Barium in the sandy soil was expected to be nearly unavailable to the test crops. Findings in this thesis provide evidences that the sand in fact contributed with a considerable part of Ba to plants. Paper II showed that white clover and bird vetch were able to take up Ba in concentrations exceeding the lowest observed effect concentration for toxicity (LOEC) reported for bush bean (Llugany et al. 2000) and Tanzanian guineagrass (Monteiro et al. 2011). The relatively high ability of the plants to absorb Ba described in Paper II was probably related to the low soil CEC and low nutrient retention ability of the sandy soil (Melo et al. 2011). This soil contained only minor amounts of both sulphur and organic matter (OM), and thus precipitation of $BaSO_4$ and adsorption of Ba to OM was limited. In soils containing high levels of sulphate, OM, or cation exchange sites, like clay, Ba is likely to be less available to plants due to e.g. sorption (Madejón 2013). The relatively low uptake of Ba in tall fescue and white clover in the second pot experiment (Paper III) compared to the first (Paper II), is possibly related to Ba precipitation with sulfate (Kabata-Pendias 2011) applied as nutrient solutions. On average tall fescue and white clover took up about 47 and 32 times more Ba from the control soil (sandy soil mixed with 5 vol% peat, and limed with NaOH) of the first pot experiment compared to the control soil of the second pot experiment, respectively (Fig. 10). Despite similar growing conditions in the greenhouse, this comparison is not fully representative. Differences in e.g. pH, length of the growth period and soil porosity most likely explain some of the variations in the element uptake between the pot experiments. However, the main difference that probably influenced the most on the Ba availability in these controls were the replacement of sulfate with chloride in some nutrient solutions in the first pot experiment to avoid $BaSO_4$ precipitation (Appendix III). In the second pot experiment about 420 mg more S per pot (as $ZnSO_4*H_2O$, $MgSO_4*7H_2O$ and K_2SO_4, see Paper II and Paper III) was added, and likely made more of the mobilized Ba precipitate as $BaSO_4$.

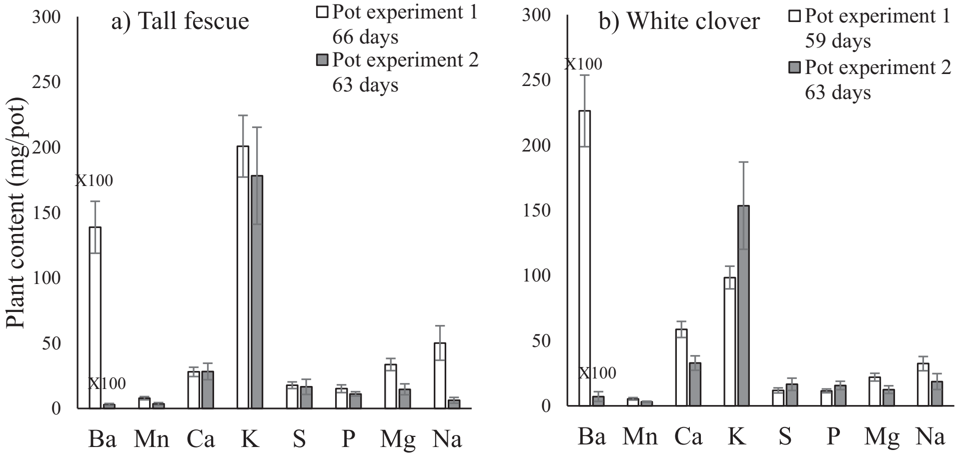


Figure 10: Total plant content (mg pot^{-1}) of selected nutrient and Ba in plants grown on control soil of pot experiment 1 and 2. In pot experiment 1 the plants were supplied with 100mL 0.075M NaOH to increase soil pH. In pot experiment 2 the plants were supplied with 50 mL 0.075M NaOH. Content of Ba has been multiplied by hundred.

The mobility of Ba seems to be largely controlled by the presence of sulphur, supported by the literature previously mentioned. Conditional to the experimental design of the second pot experiment, the mobility of Ba on increasing content of peat organic matter, and carbonatite supplied as a liming agent was determined. Possible plant Ba enrichment deriving from carbonatite is of great concern. Hence, a factorial regression was applied on the model in Table 1 to analyse the effect of plant species (white clover and tall fescue), treatment (100 g carbonatite and 42 g dolomite), and peat gradient (5, 20, and 50 vol% peat) on the Ba uptake (µg Ba pot^{-1}, log-normalized) for each harvest. Soil containing 100% peat does not contain sand, and flowingly no sand derived Ba. These pots were therefore not included in the model. The interaction between soil, plant species and treatments ($p = 0.05$, Fig. 11d), shows that the Ba mobilization and uptake to plants is controlled by both soil and plant factors. Compared to pots given dolomite, an additional increase in Ba uptake was noticed in pots treated with carbonatite ($p < 0.001$, Fig. 11c). Compared to tall fescue, the uptake of Ba in white clover was significantly higher ($p < 0.001$, Fig. 11a). The Ba uptake was increased additionally with increasing peat content in soil ($p < 0.001$, Fig. 11b). The role of these individual factors will be discussed more thoroughly in the following sections.

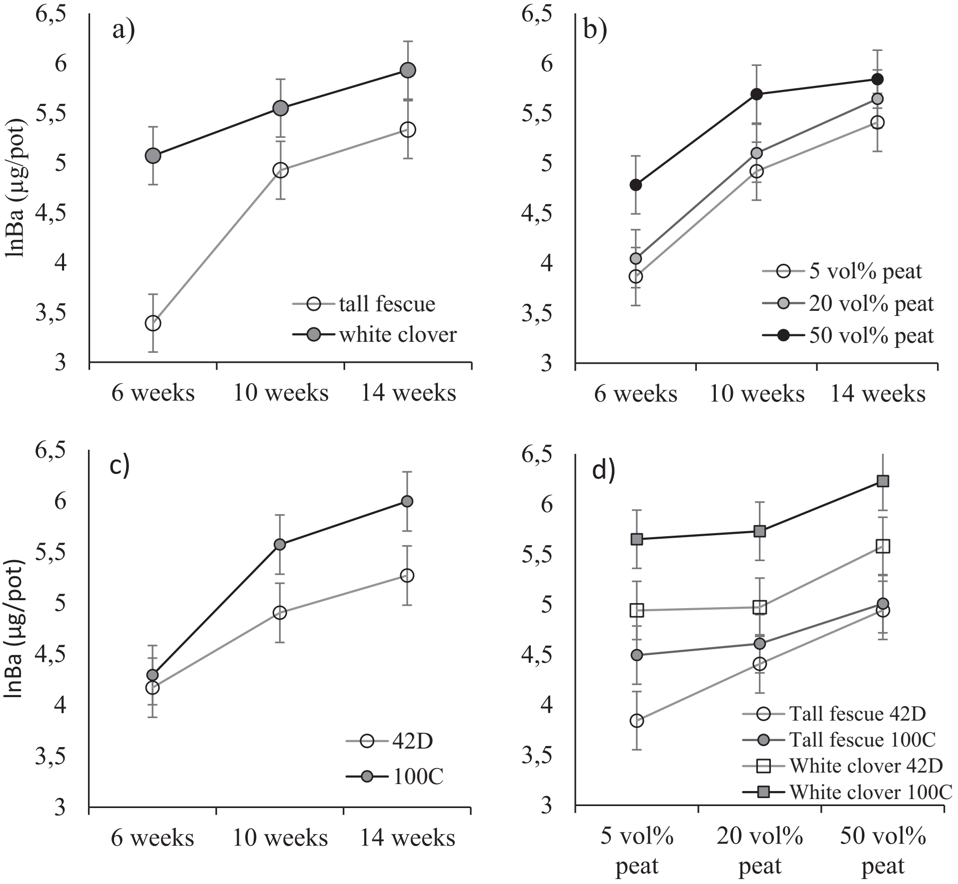


Figure 11: Effect plot for interactions between harvest and **a)** species, **b**) soil, and **c**) treatment in response to log normalized Ba content (µg/pot); **d:** Interaction between species, soil and treatment. Bars represent the pooled coefficient of variance (CV) equal to the square root of MSE obtained from the ANOVA table (table not shown). 42D = 42 g dolomite added to each pot, 100C = 100 g carbonatite added to each pot.

The design of the second pot experiment (paper III) was relatively complex, with several significant factors influencing the behaviour of Ba. To be able to address the influence of other factors, e.g. nutrients, pH, and plant dry weight, a principal component analysis (PCA) was performed. The factors of Table 1, in addition to pH, selected nutrients and plant dry weight, were included in the model to investigate the variation in uptake of Ba, Sr, Ca, Mg, and K to plants as affected by two orthogonal principal components conditional to the experimental design. The resulting biplot displayed in Fig. 3 shows that Ba, Sr and Ca uptake by plants are strongly related to the carbonatite treated pots and with white clover, while the Mg uptake is strongly related to the dolomite treated pots and with tall fescue. Potassium, dry weight and weeks are equally affected by both principal components, but in different directions (Fig. 12). Dry weight, pH, and weeks of growth are strongly related. The two principal components are strongly affected by mineral treatment (comp. 1) and test plant (comp. 2). The different symbols used to label the observations, confirm the impact of mineral treatments and test crops used, on the variation in observations quite visible. Fig. 12 exemplifies the close relationship between plants, rhizosphere, and geochemistry in soil.

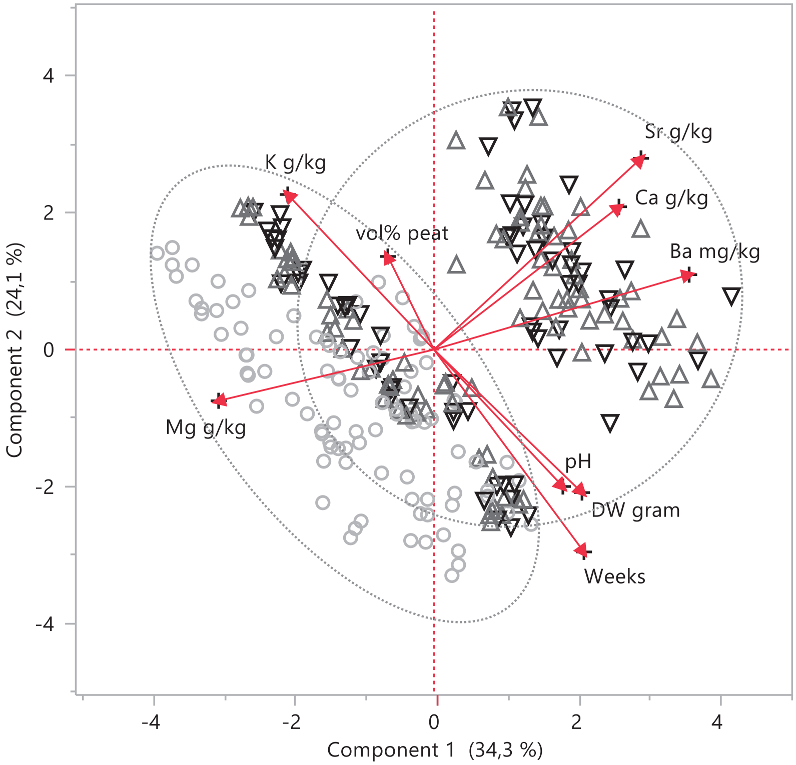


Figure 12: Biplot giving the influence of element concentration, pH, dry weight (DW), weeks of harvest and peat organic matter. Triangles represent carbonatite, and circles represent dolomite. The cluster of points is related to interactions between harvests, species, peat and treatment on element uptake. Encircled symbols top right include white clover, and encircled symbols bottom left include tall fescue.

The main findings from the geochemical analyses of Paper IV, indicate that the Ba uptake by tall fescue and white clover (second pot experiment) is mainly controlled by the exchangeable Ba-fraction in soil, in addition to the Ba weakly bound to fulvic acids (FA) in the pore water (Fig. 13). All alkaline earth elements are absorbed by plants in the ionic form (He et al. 2012). The binding of Ba^{2+} to organic matter does not necessarily mean that Ba^{2+} is unavailable to plants. The main fraction of Ba_{fa}, which was diffusively bound, may supply Ba and other cations to the pore water-root interface. There is evidence from Paper IV to suggest that Ba in pore water originate mainly from exchange sites on colloids associated with biotite, and K-feldspar, which in turn supply Ba to plant roots. These findings support the hypothesis of a colloid born Ba supply to roots from exchange sites in soil, in agreement with suggestions proposed by Lamb and colleagues (2013). Lamb and colleagues (2013) reported a significant positive relationship between the plant uptake of Ba, and Ba adsorbed to soil colloids deriving from ion exchange sites in soil. The ability of tall fescue and white clover in taking up Ba seems to overcome the Ba adsorption potential by peat. Abreu et al. (2012) have also demonstrated an increase in Ba uptake by plants on increasing supply of peat. This exemplifies that Ba might still be relatively mobile in soil (Kabata-Pendias 2011). Nevertheless, the Ba concentrations in tall fescue and white clover (Paper III) ranged from 8 to 70 and from 20 to 130 mg kg^{-1} DW, respectively. These concentrations are way below concentrations reported to induce phytotoxicity (Llugany et al. 2000; Chaudhry et al. 1977; Monteiro et al. 2011).

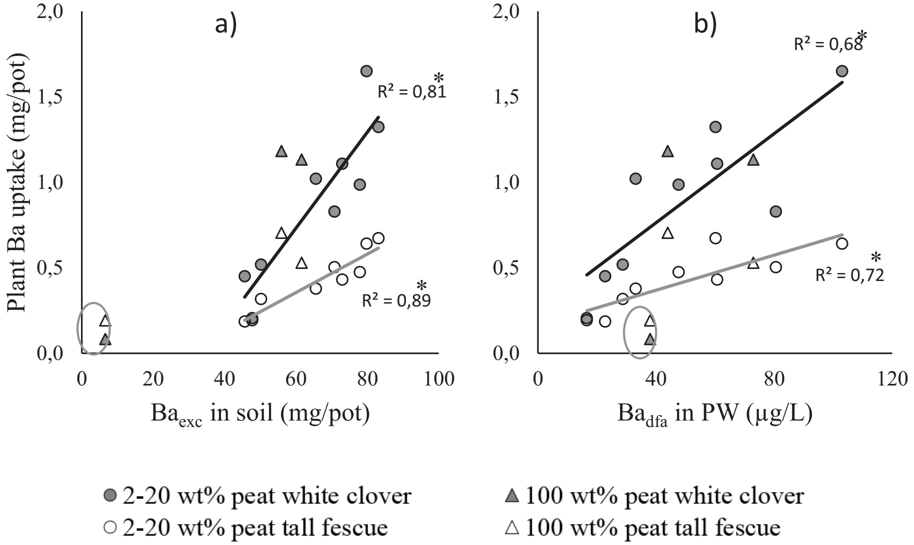


Figure 13: Total plant uptake of Ba related to a) exchangeable Ba (Ba_{exc}) in soil, and b) Ba diffusively bound to colloidal fulvic acids (Ba_{dfa}). Asterisks (*) indicate level of statistical significance >95%. Plants grown in 100% peat are separated from the regression. Encircled points lack the Ba sources (sand and carbonatite).

5.4.2 Barium acquisition potential by plants

The high variability in the transfer of elements from soil to plants is connected to both binding strengths of elements to soil (mineral), and biogeochemical differences among plant species and their acquisition for certain nutrients over others (*NORSØK*, 2003; *Gjengedal* et al., 2015). Other factors related to availability of nutrients to plants comprise e.g. pH, soil organic matter, cation exchange capacity, microbial activity, and rhizosphere activity. The "sum to zero" availability of Ba in soil, and the plants potential to take up this element from soil can fairly well be estimated by the bioconcentration factor, or transfer factor (TF, chapter 2.3.4). The main purpose by using TFs was to compare Ba bioconcentration potential between plant species grown under similar conditions. In general, the highest TFs observed for Ba in the field survey at Stjernøy (Paper I), and in both pot experiments (Paper II and IV) were noticed in herbs and/or legumes, and the lowest in grasses. The relatively moderate concentration of Ba in most plant species at Stjernøy compared to the very high total (XRF) and AL-extractable Ba concentration in soil indicate a rather low acquisition potential by plants, and high Ba retention to soil. Of the plant species investigated, the highest TFs in both Paper I and II was observed in the leguminous species bird vetch, indicating a particular ability by this plant to acquire additional Ba from non-exchangeable reserves in mineral soils. There is a limited number of studies on mechanisms controlling plant uptake of Ba from non-exchangeable sites in soil. Other experiments have shown that even in fertilized soils, with sufficient supply of K, plants can acquire near 20% of the K from non-exchangeable sites, like the interlayer of clay (Marschner 1995). The present thesis suggests this might also be the case for bird vetch, since Ba follows K in geochemical processes (Kabata-Pendias 2011). By definition, accumulation is the ability of a plant to accumulate an element to higher tissue concentrations than the concentration in the growth medium. Thus, based on findings of Paper I and II, bird vetch can be defined as a Ba accumulator. The increased TFs of Ba from soil to herbs and legumes compared to grasses indicate a general higher capacity by herbs and legumes to concentrate Ba from mineral soils (Paper I, II and IV).

Plant dependent differences and influence of microbial activity probably contribute to the large variations in uptake of nutrients and trace metals (Marscher, 2012; Aerts and Chapin, 1999; Løes et al., 1998; Cipollini and Pickering, 1986). In general, plant species with high potential for root CEC may accumulate Ba in higher amounts than other species (Cipollini and Pickering 1986). The high uptake and bioconcentration of Ba obtained in roots of gray pea described in Paper II was explained by high CEC in roots and a potential influence of rhizobium activity. Gray pea relies entirely on biological N fixation, as demonstrated by large amounts of active rhizobia nodules on the roots. Active rhizobia nodules were also noticed on roots of white clover in Paper III/IV. Since high root CEC promotes metal uptake (Prasad 2004, Prasad and Saxena 2004), further investigations on Ba uptake in legumes should focus on the influence of rhizobia-induced N fixation processes on CEC.

By expressing the plant uptake of elements as the total uptake (i.e accounting for differences in dry weight) as compared to concentration, the picture of the plants potential to acquire elements from soil may be quite different. Plant size was not considered in Paper I, and thus, dilution effects could not be determined. Even though the legumes in Paper II had notably higher concentrations of Ba than the grasses, differences in Ba acquisition potential from soil was probably low, as the total Ba content in barley did not differ from that of gray pea and white clover, and the total Ba content in tall fescue did not differ from that of bird vetch (Fig. 14). Hence, the considerable differences in Ba concentrations between bird vetch and tall fescue may have been an effect of dilution. The lower Ba concentrations in roots of radish and carrot, in contrast to spinach and gray pea, were probably related to a dilution effect, due to differing root structure. This might be confirmed by the total Ba uptake expressed in terms of DW (mg Ba pot^{-1}), which showed an opposite trend to plant Ba concentration (mg kg^{-1}, Fig. 14). The plant size of tall fescue and white clover in terms of dry weight (Paper III) was, however, relatively equal. Hence, the increased total uptake of Ba to white clover strengthens the hypothesis of an increased acquisition potential for Ba compared to tall fescue.

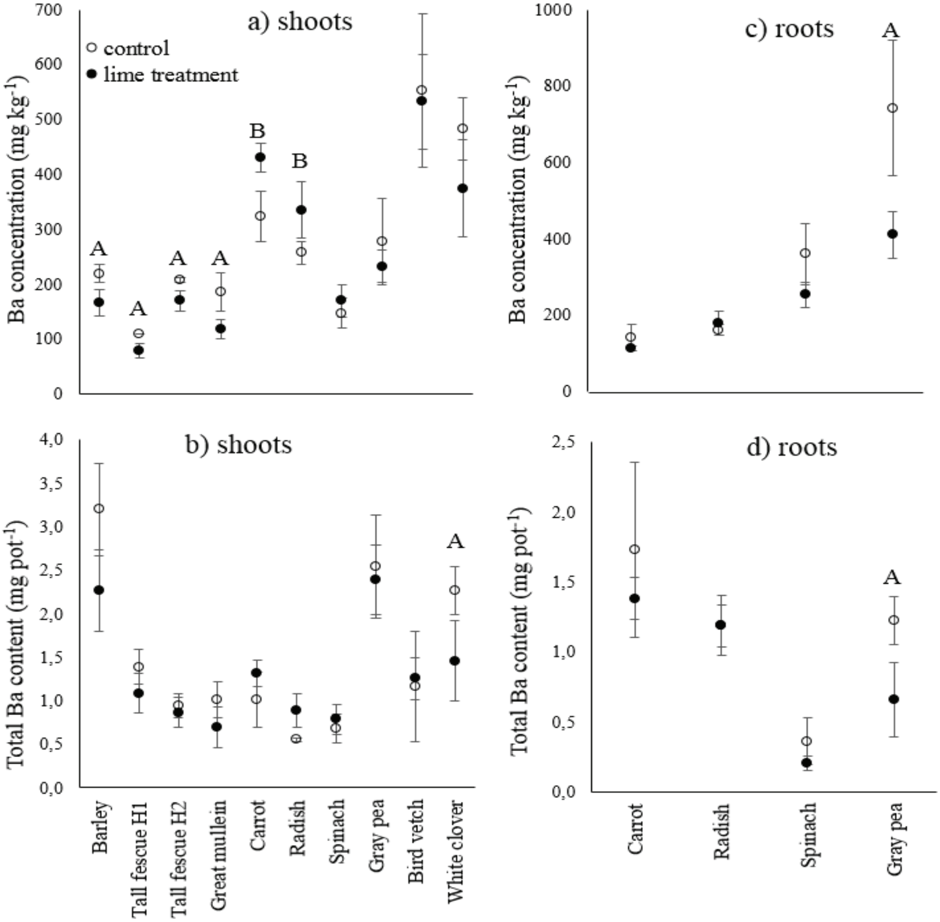


Figure 14: Effect of liming on Ba uptake from a sandy tectosilicate soil (feldspar and quartz) by vascular plants (Paper II).

None of the studies in this thesis was designed to test phytotoxicity of Ba. Considering plant species included in the present work, no toxic effect caused by Ba has been reported in literature, except for barley. The concentration of Ba in barley grain and white clover in Paper II was about 10 and 35 times higher than the concentration in the respective species reported by Kabata-Pendias (2011). Still, average shoot Ba concentration in barley (Fig. 14) was about 100-fold lower than the concentration reported to induce considerable yield decreases in barley (Chaudhry et al. 1977). However, toxic symptoms may occur internally in the plants before the plant yield is affected (e.g. Llugany et al. 2000). Despite this, the plant concentrations of Ba observed in most of the plants included in this thesis are well below concentrations reported to cause internal symptoms of toxicity (like Ba blocking of K channels in soybeans, Llugany et al. 2000). Considering future possibilities for agricultural use of carbonatite rock powder, the low uptake of Ba in grasses is advantageous, but a cause of concern is the high potential for Ba accumulation by bird vetch.

5.4.3 Relationship between Ba and Ca in plants

In the field survey at Stjernøy (Paper I), the positive correlation between Ba and Ca concentration (Fig. 15) provides strong evidence that Ba follows Ca uptake and distribution in plant tissues. Despite large variations in Ba concentrations in soil and plants, the uptake of Ba in general was only slightly reflecting the soil chemistry of the respective areas investigated. Plant species and their affinity for Ca were much more significant in explaining both Ba and Sr uptake. The alkaline earth metals Ba, Sr, Mg, and Ca have been reported to behave similarly in their accumulation in plants grown in temperate forest of Japan (Memon et al. 1983). Interactions between the alkaline earth metals are complex, and although they can compete with each other, Ba and Sr cannot replace the biochemical functions of e.g. Ca. The relationship between Sr and Ca in plants of Paper I was expected because of their geochemical relationship in the soil minerals (calcite in carbonatite, pyroxene and hornblende in the pyroxenite). Strontium is absorbed following the plants metabolic requirements for Ca and is related to both the mechanisms of mass flow and exchange diffusion (Kabata-Pendias, 2011). Findings described in Paper I suggest that the plant's uptake of Ca seem to enhance its uptake also of Ba, supporting findings of Paper II (Fig. 14 and 16) and Paper III (Fig. 12). Wallace and Romney (1971) suggested that Ba uptake to roots could be limited by the presence of Ca, due to antagonistic interactions. Based on findings in Fig. 14 this indication seems valid for plants with low acquisition for Ca, e.g. tall fescue. However, plants with a high demand for Ca is less affected by potential antagonistic effect of Ca on Ba uptake. In the work presented in Paper I and II, bird vetch took up considerable higher amounts of Ba and Ca from soils of different mineralogy compared to the other plant species, and in Paper II additional supply of $CaCO_3$ did not influence significantly on the species´ uptake of Ba (Fig. 14). As the geochemistry of nutrients in the soil-root interface was not determined in the field survey (Paper I), possible interaction of Ca on Ba uptake by roots was not considered. In general, the transfer of Ba from soil to grasses was limited, but it is unclear whether this could be connected to the high presence of Ca in soil (Paper I). To the authors´ knowledge, the literature covering the link between Ba and Ca in herbs and legumes compared to grasses is rather limited. Higher affinity for Ca by legumes and herbs compared to grasses and cereals, is reported (e.g. Loneragan and Snowball, 1969), and Robinson and colleagues (1950) reported that some leguminous species, such as alfalfa and soybean, tended to accumulate relatively large quantities of Ba compared to wheat and corn grain. This is likely controlled by uptake mechanisms in plants (e.g. Cipollini and Pickering 1986; Mitra 2015) as plants may influence on the actual uptake of an element by selective absorption of cations (Gjengedal et al. 2015; Collander 1941), but also resulting from similar geochemistry between these ions (Kabata-Pendias 2011; Marschner 2012).

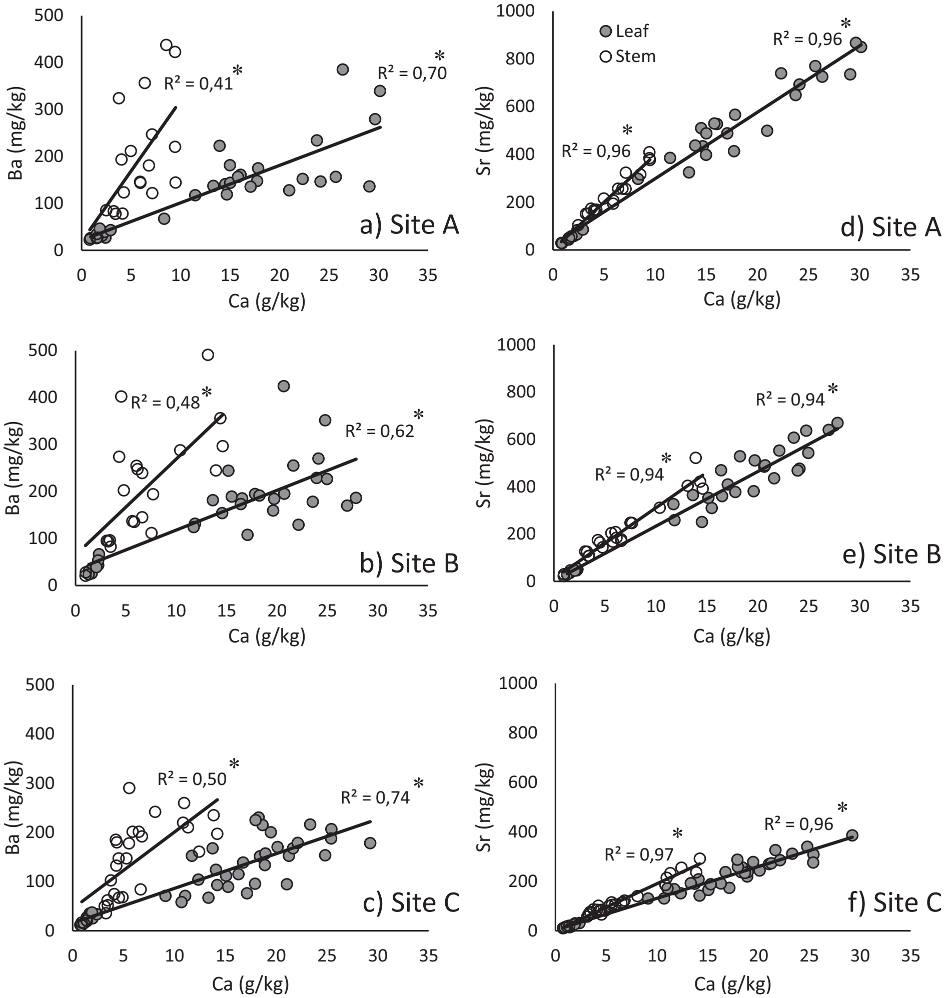


Figure 15: Concentration of strontium and barium related to calcium in leaves/shoots of 16 plant species, and associated stems of 11 of these plants, collected at site A, B, and C at Stjernøy, northern Norway (Paper I). *V. cracca* (bird vetch) is not included in the analyzed data matrix. Asterisks represent significance within a 95% confidence lever.

In general, uptake of Ba from the soil seems to be slightly suppressed by liming (Paper II), as demonstrated by the lower Ba:Ca ratio in plant tissues of lime-treated species (Fig. 16). The negative response to liming of Ba concentration in shoots of barley, tall fescue, and great mullein is in agreement with literature (Wallace and Romney 1971; Kabata-Pendias 2011). Considering tuber vegetables for food, the translocation of Ba to non-edible plant parts by liming is promising (Paper II). The general increase in Ba translocation from roots to shoots combined with the ambiguous Ba response in different plant species to liming reflects the complex relationship between the antagonistic effect of Ca on Ba transfer from soil to roots, and the distribution relationship between these two elements within plants. As Ba seems to follow Ca uptake and distribution, the high Ca affinity observed for carrot, radish, spinach, gray pea, and bird vetch may give an indication as to why Ba concentrations in shoots were not significantly depressed by liming. Paper II provides evidence to suggest that liming reduces Ba uptake in species with low affinity for Ca (Fig. 14).

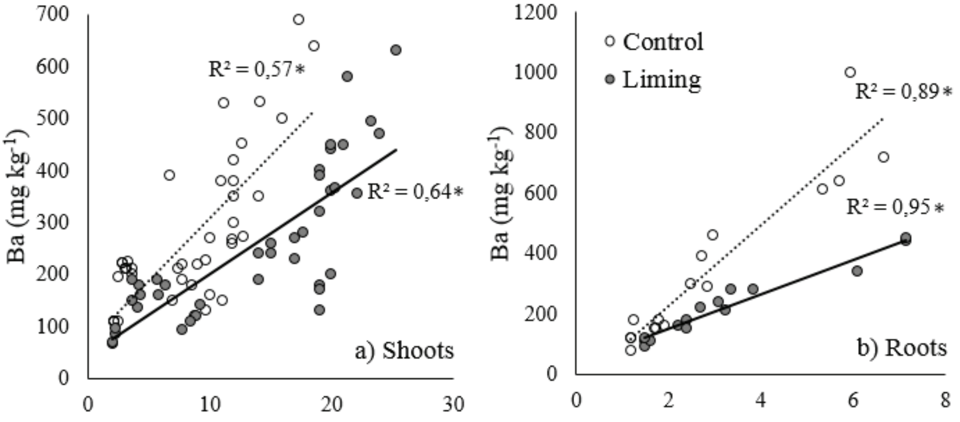


Figure 16: Relationship between Ba and Ca (Paper II) in **a)** shoots of nine plant species in the control ($F_{1,38} = 69$, $p<0.001$) and lime treatment ($F_{1,38} = 50$, $p<0.001$))); and **b)** in roots of four plant species in the control ($F_{1,14} = 116$, $p<0.001$) and lime treatment ($F_{1,13} = 252$, $p<0.001$). Effect of individual species not shown. Asterisks represent significance ($p<0.001$).

6 Conclusions and recommendations

Carbonatite rock from the Lillebukt Alkaline Complex located at Stjernøy, Norway, is proposed as a slow-release lime and rock-fertilizer, due to significant concentrations of nutrients in minerals that weather quite easily. The cause of concern is related to enrichment of the potentially biotoxic Ba, that may cause undesired uptake to plants when carbonatite is applied to agroecosystems. In the present work, processes influencing the mobilization of Ba in soils with ordinary and Ba-enriched mineralogy, and the availability of Ba to plants were investigated.

All plant species investigated in the thesis were able to take up Ba from mineral soils (carbonatite, pyroxenite or sandy tectosilicate soil). Compared to values reported in vegetation in the northern part of Europe, plant tissue concentrations of Ba measured in vegetation from Stjernøy were equally high, or higher, with median Ba values of 30, 100, and 150 mg kg^{-1} DW in grasses, dwarf shrubs and herbs, respectively. For most plant species, concentrations of Ba in plant tissues did not reflect the soil mineralogy at Stjernøy, but seemed to be mostly affected by species dependent requirements for Ca. Irrespective of growth media used in the thesis, grasses had the lowest Ba uptake, which is advantageous, regarding the use of carbonatite rock powder as fertilizer or soil amendment. Herbs and legumes concentrated significantly more Ba in comparison. The leguminous species *Vicia cracca* (bird vetch) is proposed to act as an accumulator of Ba, with its exceptionally high tissue concentrations, reaching 2000 mg kg^{-1} DW when grown on carbonatite soil, and 600 mg kg^{-1} when grown on sandy tectosilicate soil. Low contents of OM, sulphur and CEC in the tectosilicate soil gave a low nutrient adsorption potential, which probably facilitated direct plant absorption of exchangeable Ba, causing Ba to concentrate in white clover and bird vetch to concentrations above those reported to cause phytotoxicity. Adding soluble S as nutrient solutions to this particular soil probably made a large fraction of the available Ba precipitate as the nearly unavailable compound $BaSO_4$. Hence, Ba uptake by plants was significantly reduced by increased application of soluble S. Common to all the experiments in the present thesis, plant tissue concentrations of Ba and Ca correlated well, supporting the hypothesis that Ba follows Ca uptake in plants.

Application of $CaCO_3$ lime to sandy tectosilicate soil decreased shoot Ba concentrations mainly in species with low affinity for Ca, i.e. tall fescue, barley, and great mullein, but no reduction was detected in plants with higher demand for Ca, like bird vetch. Carbonatite was a significant source to plant Ba when applied to the tectosilicate sandy soil as a liming agent. In general, carbonatite was unable to buffer the pH drop by additional supply of peat, but the plant dry weight was unaffected. The uptake of Ba to tall fescue and white clover was further amplified by increasing the supply of peat, probably due to increased weathering of carbonatite and K-feldspar minerals by organic acids. Such peat amendments enhanced weakly bound colloidal Ba in the pore water, thereby increasing the amount of available Ba to the test crops. Barium was mainly taken up from the exchangeable Ba fractions in soil, and Ba diffusively bound to colloids in pore water. Moreover, DGT measurements showed that white clover mobilized Ba more effectively from soil than tall fescue, supporting the hypothesis of an active plant factor in the rhizosphere, and a species dependent Ba acquisition potential. Nonetheless, the Ba concentration in tall fescue and white clover grown on soils amended with carbonatite and supplied with soluble S ranged from about 8 to 70 mg kg^{-1} and 20 to 130 mg kg^{-1}, respectively, and were considerably lower than concentrations reported to induce phytotoxicity symptoms.

In the present work, the relatively moderate Ba uptake by plants grown on soils amended with carbonatite is promising when considering carbonatite as a lime and rock fertilizer. However, caution needs to be addressed to highly weathered soils, or soils with high contents of organic acids and little sulphur, as Ba may accumulate in plants with particular demand for Ca or in plants with a Ba accumulation potential. Applications of high amounts of carbonatite to soil, combined with relatively low uptake by most plants may cause Ba to accumulate in the soil. Long-term effects of carbonatite supply to agricultural soils in field trials should be considered, as well as the associated impact of climatic conditions, leaching and run-off on the fate and behaviour of Ba. The present work shows the importance of investigating different groups of vascular plants due to interspecies differences in Ba acquisition potential and distribution strategies. The increased DGT-available Ba in pots containing white clover call for further investigation on rhizosphere activity by dicots, and possible microbial impact on the mobilization of Ba compounds in soils. Barium mobility in mineral soils seem to be largely controlled by e.g. organic acid content, cation exchange capacity, sulphate, and rhizosphere activity. Influence of clay content, and anaerobic conditions on the mobilization and availability of Ba from carbonatite applied to soils should be considered in further trials. A risk of Ba accumulation in certain forage legumes grown in soils naturally rich in Ba, emphasise that further research on toxicity when carbonatite is applied to agricultural soils is required.

7 References

Aasen, I. (1997): Mangelsjukdomar og Andre Ernæringsforstyrringar hos Kulturplanter. Second Ed. Landbruksforlaget, Norway. 95 pp.

Abreu, C. A., Cantoni, M., Coscione, A. R., Paz-Ferreiro, J. (2012): Organic matter and barium absorption by plant species grown in an area polluted with scrap metal residue. *Applied Environ. Soil Sci.* 2012, 1-7.

Adriano, D. C. (2001): Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and risks from metals. Second Ed. New York, Springer-Verlag, 867 pp.

Aerts, R. Chapin, F. S. (1999): The Mineral Nutrition of Wild Plants Revisited: A Re-evaluation of Processes and Patterns. Adcances in Ecological Research. Vol. 30. 67 pp.

Almås, Å. R., Lofts, S., Mulder, J., Tipping, E. (2006): Solubility of major cations and Cu, Zn and Cd in soil extracts of some contaminated agricultural soils near a zinc melter in Norway: modelling with a multisurface extension of WHAM. *European J. Soil Sci*. 58, 1074-1086.

Agency of Toxic substances and Disease Registry, ATSDR (2007): Toxicological Profile for Barium and Barium Compounds. U.S. Department of Health and Human Services. Available at: http://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=327&tid=57.

Anderson, D. W. (1988): The effect of parent material and soil development on nutrient cycling in temperate ecosystems. *Biogeochemistry*. 5, 71-97.

Bakken, A. K., H. Gautneb, and K. Myhr (1997): The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. *Nutr. Cycl. Agroecosyst.* 47, 8.

Bakken, A. K., H. Gautneb, T. Sveistrup, and K. Myhr (2000): Crushed rocks and mine tailings applied as K fertilizers on grassland. *Nutr. Cycl. Agroecosyst.* 56.

Bettencourt, A. O., Teixeira, M. M. G. R., Elias, M. D. T., Faisca, M. C. (1988): Soil to plant transfer of Radium-226. *J. Environ. Radioact*. 6, 49-60.

Boffito, C. (1991): Barium. *Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition.* 3, 7 pp.

Bonito, M., Breward, N., Crout, N. M. J., Smith, B., Young, S. D. (2008): Chapter 10: Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils : operational and technical aspects. In: Vivo, B., Belkin, H. E., Lima, A., (eds.). *Environmental Geochemistry: Site Characterization, Data Analysis and Case Histories.* London, UK, Elsevier, 213-249, 429 pp.

Bormann, F. H., Likens, G. E. (1967): Nutrient cycling. *Science* 155 (3761), 424-429.

Bray, R. H., and L. T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Science* 59:39–45.

Brazilian national environment council (2006) Resolution #375, August 30, 2006. Available at: http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=506 (in Portuguese).

Brazilian national environment council (2009): Resolution #420, December 28, 2009. Available at: http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620 (in Portuguese).

Brown, C. E. (1998): Applied multivariate statistics in geohydrology and related sciences. Berlin Heidelberg: Springer, Germany, 248 pp.

CCME (2013): Canadian Soil Quality Guidelines for barium. *Protection of Human Health Scientific Criteria Document*.

Chaudhry, F. M., A. Wallace, and R. T. Mueller (1977): Barium toxicity in plants. *Commun. Soil Sci. Plant Anal.* 8, 795.

Chojnacka, K., Chojnacki, A., Górecka, H., Górecki, H. (2005): Bioavailability of heavy metals from polluted soils to plants. *Sci. tot. Environ*. 337, 175-182.

Choudhury, H, and R. Cary (2001): Barium and Barium Compounds. Concise international chemical assessment document 33. WHO. Available at: www.inchem.org/documents/cicads/.../cicad33.htm.

Cipollini, M. L., Pickering, J. L. (1986): Determination of the phytotoxicity of barium in leach-field disposal of gas well brines. *Plant Soil.* 92, 159-169.

Collander, R. (1941): Selective absorption of cations by higher plants. *Plant Physiol.* 4, 691-720.

Corfu, F., Roberts, R. J., Torsvik, T. H., Ashwal, L. D., Ramsay, D. M. (2007): Peri-gondwanan elements in the Caledonian nappes of Finnmark, Northern Norway: implications for the paleogeographic framework of the Scandinavian Caledonides. *American J. Sci.* 307, 434-458.

Coscione, A. R., Berton, R. S. (2009): Barium extraction potential by mustard, sunflower and castor bean. *Sci. Agric.* (Piracicaba, Braz.) 66 (1), 59-63.

Cottenie, A., Camerlynck, R., Verloo, M., Dhaese, A. (1980): Fractionation and determination of trace elements in plants, soils and sediments. *Pure Applied Chemistry*. 52 (1), 45-53.

Cuypers, A., Remans, T., Weyems, N., Colpaert, J., Vassilev, A., Vangronsveld, J. (2013): Soil-Plant Relationships of Heavy Metals and Metalloids. In: Alloway -Heavy Metals in Soils -Trace Metals and Metalloids in Soils and their Bioavailability. Third Ed. Environ. Poll. 22. 615 pp.

Davis, R. D., P. H. T. Beckett, and E. Wollan (1978): Critical levels of twenty potentially toxic elements in young spring barley. *Plant Soil* 49, 395.

Davison, W., Zhang, H. (1994): In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*, London. 367, 546-548.

DiBello, P. M., J. L. Manganaro, and E. R. Aguinaldo (1991): Barium compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th Edition. *John Wiley and Sons, New York, Chichester, Brisbane, Toronto and Singapore* 3, 22.

Dotaniya, M. L., Meena, V. D. (2015): Rhizosphere effect on nutrient availability in soil and its uptake by plants: a review. *Proc. Natl. Acad. Sci., India, Sect. B Biol. Sci.* 85 (1), 1-12.

Egnér, H., Riehm, H., Domingo, W. R. (1960): Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor- und Kaliumbestimmung. *KungligaLantbrukshögskolans annaler* **26**. pp.199-215.

Essington, M. E. (2004): Soil and Water Chemistry: An Integrative Approach. Chapter 10 Acidity in Soil Materials. 474 pp.

Faraway, J. J. (2002): Practical regression and anova using R. Available at: http://www.mathstat.ualberta.ca/~wiens/stat568/misc%20resources/Faraway-PRA.pdf.

Finck, A. (1982): Fertilizers and fertilization. Verlag Chemie, Weinheim, Germany, 438 pp.

Fyfe, W. S., Leonardos, O. H., Theodoro, S. H. (2006): Sustainable farming with native rocks: the transition without revolution. *Braz. Acad. Sci.* 78 (4), 715-720.

Garmo, Ø. A., Røyset, O., Steinnes, E., Flaten, T. P. (2003): Performance study of diffusive gradients in thin films for 55 elements. *Anal. Chem.* 75, 3573-3580.

Gautneb, H. (2009): Review of the geology and the apatite distribution of the carbonatite in the Lillebukt Alkaline Comples, Stjernøy Northern Norway. *Geological Survey of Norway* Report no. 2009.061. 33 pp.

Gautneb, H., Bakken, A. K. (1995): Crushed rocks, minerals and mine tailings as sources of potassium in agriculture. *NGU-Bull*. 427. 119-122.

Gjengedal, E., Martinsen, T., Steinnes, E. (2015): Background levels of some major, trace, and rare earth elements in indigenous plant species growing in Norway, and the influence of soil acidification, soil parent material, and seasonal variation on these levels. *Environ. Monit. Assess*. 187, 1-28.

Harley, A. D., Gilkes, R. J. (2000): Factors influencing the release of plant nutirent elements from silicate rock powders: a geochemical overview. *Nutr. Cycl. Agroecosyst.* 56, 11-36.

He, H., T. M. Bleby, E. J. Veneklaas, H. Lambers, and J. Kuo (2012): Precipitation of calcium, magnesium, strontium and barium in tissues of four Acacia species (Leguminosae: mimosoideae). *PLoS ONE* 7.

Heier, K. S. (1961): Layered gabbro, hornblendite, carbonatite and nepheline syenite on Stjernøy, North Norway. *Norsk Geol. Tidskr.* 41.

Heier, K. S. (1962): Trace elements in feldspars -a review. *Norsk Geol. Tidsskr*. 42 (2): 415-466.

Heim, M. (2001): Norsk steinmel til (øko-)landbruk: historikk, status quo, utfordringer og muligheter. In: Sammendrag fra Nordisk Mineralsymposium "Verdiskapning fra mineral til ferdig produkt". Trondheim 23.-24.april 2001, 6.

Heim, M., Hillersøy, M. H., Bleken, M. A., Gautneb, H., Gjengedal, E. (2012): Apatite-biotite-carbonatite (Stjernøy, N-Norway) -Potential and obstacles regarding a multinutrient rock-fertilizer. *10th International congress for applied mineralogy (ICAM)*, 8.

Hillersøy, M. (2010): Plant uptake of Barium and Strontium in areas with biotite-carbonatite bedrock at Stjernøy, Alta, Norway. *Master thesis; Norwegian University of Life Sciences*.

Hooda, P. S., Zhang, H., Davison, W. and Edwards, A. C. (1999): Measuring bioavailable trace metals by diffusive gradients in thin films (DGT): soil moisture effects on its performance in soils. European J. Soil Sci., 50(2), 285-294.

Jianu, D., Iordache, V., Soare, B., Petrescu, L., Neagoe, A., Iacob, C., Orza, R. (2012): The Role of Mineralogy and Geochemistry in Hazard Potential Assessment of Mining Areas. In: Kohte, E., Varma, A Bio-Geo Interactions in Metal-Contaminated Soils. Soil Biology 31. pp. 35-79.

Jolly, Y. N., Islam, A., Akbar, S. (2013): Transfer of metals from soil to vegetables and possible health risk assessment. *SpringerPlus*. 2: 385, 1-8.

Jones, J. B. (1999) Soil Analysis Handbook of Reference Method. Soil and Plant Analysis Council Inc. CRC Press. pp. 264.

Kabata-Pendias, A. (2011): Trace Elements in Soils and Plants. Fourth edition. *Taylor and Francis Group*.

Klemsdal (2010): The eolian landforms and sediment in the valley of River Jømna, east of Elverum, south-east Norway. *Norsk Geografisk Tidsskrift -Norwegian Journal of Geography*, 64 (2), 94-104.

Krogstad, T. (1992): Methods of Soil Analyses, Report no. 6/92: In Norwegian only. Institute of Environmental Science. NMBU, Norway. 32 pp.

Lagas, P., Loch, J. P. G., Bom, C. M., Gerringa, L. J. A. (1984): The behavior of barium in a landfill and the underlying soil. *Water Air Soil Poll*. 22, 121-129.

Lamb, D. T., Matanitobua, V. P., Palanisami, T., Megharaj, M., Naidu, R. (2013): Bioavailability of barium to plants and invertebrates in soils contaminated by barite. *Environ. Sci. Technol*. 47, 4670-4676.

Lee, S. S., Nagy, K. L., Fenter, P. (2007): Distribution of barium and fulvic acid at the mica-solution interface using in-situ X-ray reflectivity. *Geochim. Cosmochim. Acta.* 71, 5763-5781.

Leonardos, O. H., Fyfe, W. S., Kronberg, B. I. (1987): the use of ground rocks in laterite systems: an improvement to the use of conventional soluble fertilizers? *Chem. Geol*. 60, 361-370.

Lid, J., Lid, D. T. (1994): Norsk Flora -Norwegian Flora. 6th Ed. Det Norske Samlaget, Oslo, Norway (In Norwegian).

Lito-project – Geochemical mapping of Norwegian bedrock (2010): Database at Geological Survey of Norway. Available at: http://www.ngu.no/lito/.

Llugany, M., Poschenrieder, C., Barceló, J. (2000): Assessment of Barium Toxicity in Bush Beans. *Arch. Environ. Contam. Toxicol.* 39, 5.

Loneragan, J. F., Snowball, K. (1969): Calcium requirements of plants. *Aust. J. Agric. Res*. 20, 465-477.

Løes, A., and A. Øgaard (1997): Changes in the nutrient content of agricultural soil on conversion to organic farming in relation to farm-level nutrient balances and soil contents of clay and organic matter. *Acta Agric. Scand., Section B -Soil Plant Sci*. 47 (4), 201-214.

Løes, A. K., Hansen, S., Eltun, R., Korsæth, A., Nordheim, O. (1998): Fosfor of kalium i jord, og næringsbalanser ved økologisk, integrert og konvensjonell dyrking. Resultat fra dyrkingssystem-forsøket på Apelsvoll forskingssenter 1990-1996. Norwegian Institute of Crop Research (Planteforsk), Report 2, 33 pp (In Norwegian).

Macnicol, R. D., and P. H. T. Beckett (1985): Critical tissue concentrations of potentially toxic elements. *Plant Soil* 85, 107.

Madejón, P. (2013): Barium, in: Alloway 2013: Heavy Metals in Soils -Trace Metals and Metalloids in Soils and their Bioavailability. Third Edition. *Environmental Pollution. Springer* 22.

Marschner, H. (1995): Chapter 13 Nutrient Availability in Soils in: Mineral Nutrition of Higher plants Second Edition. *Institute of Plant Nutrition, University of Hohenheim. Germany. Academic Press. Harcourt Brace and Company*. ISBN: 978-0-12-473542-2.

Marschner, P. (2012): Mineral Nutrition of Higher Plants Third Edition. School of Agriculture, Food and Wine. The University of Adelaide, Australia.

Mazoyer, M., Roudart, L. (2006): A History of World Agriculture from the Neolithic Age to the Current Crisis. New York: Monthly Review Press. 496 pp.

McGrath, S. P., Chang, A. C., Page, A. L., Witter, E. (1994): Land application of sewage sludge: scientific perspectives of heavy metal loading limits in Europe and the United States. *Environ. Reviews* 2 (1), 108-118.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis* 15: 1409–1416.

Melo, L. C. A., Alleoni, L. R. F., Carvalho, G., Azevedo, R. A. (2011): Cadmium- and barium-toxicity effects on growth and antioxidant capacity of soybean (Glycine max L.) plants, grown in two soil types with different physicochemical properties. *Journal of Plant Nutr. Soil Sci.* 174, 847.

Memon, A. R., T. Kuboi, K. Fujii, S. Ito, and M. Yatazawa (1983): Taxonomic character of plant species in absorbing and accumulation alkali and alkaline earh metals grown in temperate forest of Japan. *Plant Soil* 70, 367.

Menzie, C. A., Southworth, B., Stephenson, G., Feisthauer, N. (2008): The importance of understanding the chemical form of a metal in the environment: the case of barium sulfate (barite). *Human Ecol. Risk Assess: An International Journal*, 14 (5), 974-991.

Mitra, G. N. (2015): Regulation of Nutrient Uptake by Plants -A Biochemical and Molecular Approach. Springer New Delhi, India. 209 pp.

Monteiro, F. A., Nogueirol, R. C., Melo, L. C. A., Artur, A. G., Rocka, F. (2011): Effect of barium on growth and macronutrient nutrition in Tanzania guineagrass grown in nutrient solution. *Commun. Soil Sci. Plan*. 42, 1510-1520.

Montgomery, D. C. (2009): Design and Analysis of Experiments, 7th Edition. International Student Version. John Wiley and Sons, Inc. ISBN: 978-0-470-39882-1. 656 pp.

Nelson, D. W., Sommers, L. E. (1982): Total Carbon, Organic Carbon and Organic Matter. Ch. 29, 539-579. In: Page, A. L., Miller, R. H., Keeney, D. R. (red.): Methods of Soil Analysis Part 2 Agronomy 9, 2th Ed., American Society of Agronomy, Inc., Madison, Wisconsin, USA. pp. 1159.

Newman, M. C., Jagoe, C. H. (1994): Inorganic toxicants -ligands and the bioavailability of metals in aquatic environments. In: Hamelink, J. L., Landrum, P. F., Bergman, H. L., Benson, W. H. (eds.), Bioavailability -Physical, Chemical and Biological Interactions, SETAC Spec. Pub. Series: CRC Press, Inc., Boca Raton, Fla., pp. 39-61.

NORSØK (2003): Økologisk Handbok- Jordkultur og Næringstilgang. Fagredaktør: Serikstad, G. L. GAN Forlag AS, Oslo, Norway. ISBN 82-492-0460-3.

Olsen S, Cole C, Watanabe F, Dean L (1954): Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular Nr 939, US Gov. Print. Office, Washington, D.C. 1-19.

Peterson, P. J., Alloway, B. J. (1979): Cadmium in Soils and Vegetation. In: The Chemistry, Biochemistry and Biology of Cadmium, Webb, M. *ed*. New York, Elsevier.

Pohanish, R. P. (2012): Sittig´s Handbook of Toxic and Hazardous Chemicals and Carcinogens. Sixth Ed. William Andrew publisher. Elsevier Inc. ISBN: 978-1-4377-7869-4. 3040 pp.

Prasad, M. N. V. (2003): Phytoremediation of Meta-Polluted Ecosystems: Hype for Commercialization. *Russian Journal of Plant Physiology* 50, 14.

Prasad, M. N. V. (2004): Heavy Metal Stress in Plants -From Biomolecules to Ecosystems. Second Ed. Springer-Verlag Berlin, Germany. 461 pp.

Prasad, M., Saxena, S. (2004): Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent. *Ind. Eng. Chem. Res*. 43, 1512-1522.

Purdey, M. (2004): Chronic barium intoxication disrupts sulphated proteoglycan synthesis: a hypothesis for the origins of multiple sclerosis. *Medical hypotheses*. 62, 746-754.

Raven, P. H., Evert, R. F., Eichhorn, S. E. (1999): Biology of Plants. Sixth Ed. W.H. Freeman and Company Worth Publishers. 944 pp.

Reimann, C., Koller, F., Frengstad, B., Kashulina, G., Niskavaara, H., Englmaier, P. (2001): Comparison of the element composition in several plant species and their substrate from a 1 500 000-km^2 area in Northern Europe. *Sci. Tot. Environ*. 278, 87-112.

Rengel, Z., Marschner, P. (2005): Nutrient availability and management in the rhizosphere: exploiting genotypic differences. Research review. *New Phytologist*. 168: 305-312.

Roberts, R. J., Corfu, F., Torsvik, T. H., Hetherington, C. J., Ashwal, L. D. (2010): Age of alkaline rocks in the Seiland Igneous Province, Northern Norway. *J. Geolog. Soc*. London, 167, pp. 71-81. Doi: 10.1144/0016-76492009-014.

Robinson, W. O., R. R. Whetstone, and G. Ergington (1950): The Occurrence of Barium in Soils and Plants. *U.S Department of Agriculture Technical Bulletin* 1013, 1-36.

SAS Institute Inc. (2013): JMP®, Version 11.1.1. SAS Institute Inc., Cary, New York.

Schielzeth, H., Nakagawa, S. (2013): Nested by design: model fitting and interpretation in a mixed model era. *Methods in Ecology and Evolution*. 4, 14-24.

Schollenberger, C. J., Simon, R. H. (1945): Determination of exchange capacity and exchangeable bases in soil- ammonium acetate method. *Soil Sci.* 59, 13-24.

Shivay, Y. S., Krogstad, T., Singh, B. R. (2010): Mineralization of copper, manganese and zinc from rock mineral flour and city waste compost for efficient use in organic farming. *Plant Soil* 326, 11.

Smith, E., Hamilton-Taylor, J., Davison, W., Fullwood, N. J., McGrath, M. (2004): The effect of humic substances on barite precipitation-dissolution behaviour in natural and synthetic lake waters. *Chem. Geol.* (2004), 81-89.

Smith, K. S., Huyck, H. L. O. (1999): An Overview of the Abundance, Relative Mobility, Bioavailability, and Human Toxicity of Metals. In: Reviews in Economic Geology. Vol 6A and 6B. The Environmental Geochemistry of Mineral Deposits. Society of Economic Geologists, Inc. (SEG). 45 pp.

Sposito, G. (1989): The Chemistry of Soils. Oxford University Press, New York.

Suwa, R., Jayachandran, K., Nguyen, N. T., Boulenouar, A., Fujita, K., Saneoka, H. (2008): Barium Toxicity Effects in Soybean Plants. *Arch. Environ. Contam. Toxicol.* 55, 7.

Tagami, K., Uchida, S. (2009): Radium-226 transfer factor from soils to crops and its simple estimation method using uranium and barium concentrations. *Chemosphere.* 77, 105-114.

Tack, F. M. G., Verloo, M. G. (1995): Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *Internat. J. Environ. Anal. Chem.* 59 (2-4), 225-238.

Tipping, E. (1994): WHAM –a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comp. Geosci*. 20, 973-1023.

Tipping, E. (1998): Humic Ion-Binding Model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aq. Geochem.* 4, 3–48.

Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M. R., Lofts, S., Hill, M. T. R., Farago, M. E., Thornton, I. (2003): The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environ. Poll*. 125 (2003), 213-225.

Tome, F. V., Rodríguez, M. P. B., Lozano, J. C. (2003): Soil-to-plant transfer factors for natural radionuclides and stabble elements in a Mediterranean area. *J. Environ. Radioact*. 65, 161-175.

Trudgill, S. T. (1977): Soil and Vegetation Systems. Oxford University Press, London, 180 pp.

United States Environmental Protection Agency, USEPA (2009): Barium in: National Primary Drinking Water Regulation Table. Available at: https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulation-table.

Van Straaten, P. (2002): Rocks for Crops: Agrominerals of sub-Saharan Africa. ICRAF, Nairobi, Kenya. 338 pp.

Van Straaten, P. (2006): Farming with rocks and minerals: challenges and opportunities. *Anais da Academia Brasileira de Ciências* 78(4), 17.

Wallace, A., Romney, E. M. (1971): Some interactions of Ca, Sr and Ba in plants. *Agron. J.* 63, 245-248.

Withers, P. J. A., Neal, C., Jarvie, H. P., Doody, D. G. (2014): Agriculture and eutrophication: where do we go from here? *Sustainability*. 6, 5853-5875.

World Health Organization, WHO (2004): Barium in Drinking Water. In: Guidelines for Drinking-Water Quality. Vol. 1: Third Ed. Geneva. 310-311.

Yara (2015): Gjødselhåndbok 2014/2015. Norwegian fertilizer handbook. Yara Norway AS. Oslo. Norway. Available at: https://yaraurl.com/hnd0.

Zhang, H., Davison, W., Knight, B., McGrath, S. (1998): In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT. *Environmental Science and Technology*, 32, 704-710.

Zhang, P. C., Brady, P. V., Arthur, S. E., Zhou, W. Q., Sawyer, D., Hesterberg, D. A. (2001): Adsorption of barium(II) on montmorillonite: an EXAFS study. *Colloids and Surfaces A: Physicochem. Engin. Aspects*. 190, 239-249.

Zhang, H., Davison, W. (2015): Use of DGT for studies of chemical speciation and bioavailability, *Environ. Chem.* 12, 85-101.

Zimmerman, A. J., Weindorf, D. C. (2010): Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures. *Internat. J. Anal. Chem.* 2010, 1-7.

Øgaard, A. F., Krogstad, T., Lunnan, T. (2002): Ability of some Norwegian soils to supply grass with potassium –soil analyses as predictors of K supply from soil. *Soil Use Manage*. 18, 412-420.

Appendix I

Table a: Overview of the analysis of acid extracted and total element concentration in the soil components used in the pot experiments (Paper II, III and IV). The pH and TOC of each soil component.

	ABC rock powder (III/IV)			Eolian sand (II-IV)			Peat (III/IV)	Peat (II)	Dolomite (III/IV)	
	XRF-analysis	ICP-MS		XRF-analysis	ICP-OES		ICP-MS	ICP-OES	ICP-MS	
		(HNO_3+HF)	HNO_3		(HNO_3+HF)	HNO_3	HNO_3	(HNO_3+HF)	(HNO_3+HF)	HNO_3
Element	n=3	n=6		n=3	n=8	n=8	n=4	n=4	n=4	
	(mg kg^{-1})	(g kg^{-1})		(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	
Ba	2500 ±140	0.60 ±0.17	2.4 ±0.40	500 ± 6	350 ±12	88 ±7.2	3.8 ± 0.10	26 ±6.8	12 ±2.2	7.0 ±0.1
Sr	3740 ± 72	2.10 ±0.09	3.9 ±0.67	76.6 ± 0.25	43 ±4.5	23 ±4.7	-	7.8 ±1.7	120 ±0	62 ±2.6
Ca	-	34 ±2.5	200 ±30	-	2 400 ±450	2 400 ±580	-	1 300 ±240	230 ±5a	15 ±0.5a
Mg	-	21 ±1.5	23 ±4.5	-	540 ±82	2 300 ±230	-	440 ±80	130 ±0a	58 ±4.0a
K	-	23 ±3.1	26 ±5.7	-	19 600 ±480	3 300 ±300	-	450 ±130	<LOD	<LOD
P	-	24 ± 8.0	5 ±2.3	-	240 ±35	280 ±64	-	140 ±36	78 ±5.0	84 ±8.1
S	-	0.45 ±0.06	0.30 ±0.11	-	<LOD	<LOD	-	520	40 ±18	<LOD
pH	9.3			4.7			3.8		9.5	
TOC (%)	4.5			0.015			51		12.6	

HNO_3 = minimum 65 w/w% sub-boiled ultra-pure nitric acid. HF = 48 w/w% hydrogen fluoride. a = g/kg.

XRF = x-ray diffraction technique (www.acmelabs.com).

TOC = total organic carbon measured by Leco TruSpec analyzer.

Appendix II

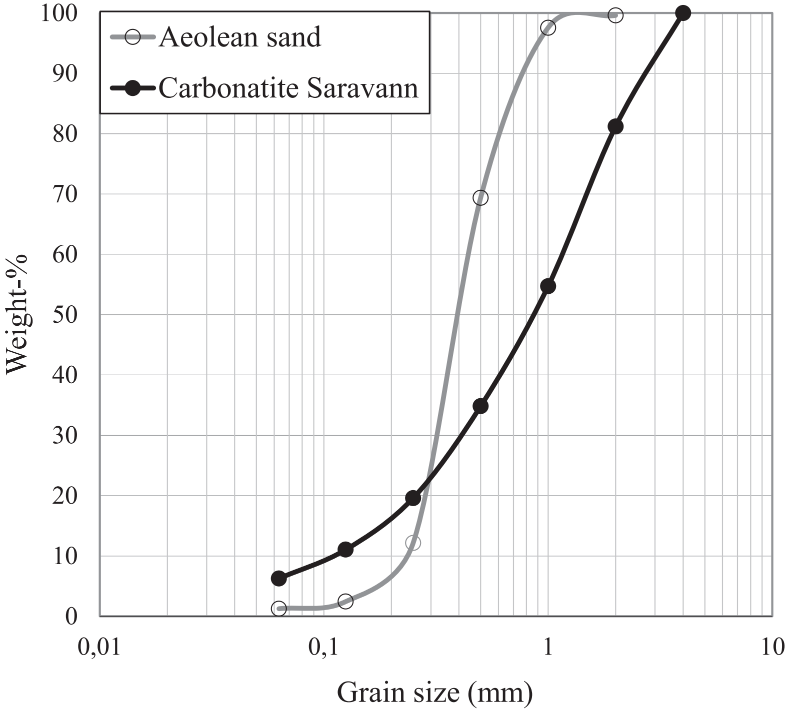


Figure a: Cumulative grain size distribution of the soil minerals used in the pot experiments (Data and illustration adopted from Michael Heim).

Appendix III

Table b: Amount of macro and micronutrient initially applied to all the pots in the first (Paper II) and second pot experiment (Paper III/ IV). In the second pot experiment, additional doses were added after the first and the second harvest (with some exceptions, see Paper III/IV).

Nutrient solutions	Concentration (g/L)	Paper II (mL)	Paper III and IV (mL)
$FeSO_4$ x7aq	5 g ch/L	25	25
$(NH_4)_6Mo_7O_{24}$ x4aq	0.05 g ch/L	25	25
$MnSO_4$ x1aq	5 g ch/2L	25	25
$CuSO_4$ x5aq	5 g ch/2L	25	25
$ZnSO_4$ x1aq	3 g ch/2L	-	25
$Na_2B_4O_7$ x10H_2O	0.5 g ch/2L	25	25
$MgSO_4$ x7aq	12.5 g ch/L	-	25
K_2SO_4	12 g K/L	-	25
$Ca(H_2PO_4)$ xaq	S g P/L	10a, 20b	25
$Ca(NO_3)_2$ x 4aq	12 g N/L	-	15b, 25a
ZnCl xaq	2.5 g ch/L	10	-
MgCl	12.5 g ch/L	25	-
KCl	12 g K/L	7.5a, 12.5b	-
NH_4NO_3	12 g N/L	15	-

a = *Festuca arundinácea*, b = *Trifolium repens*, ch = chemical

Paper I

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Uptake of macro nutrients, barium, and strontium by vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway

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Abstract

Carbonatite originating from the Lillebukt Alkaline Complex at Stjernøy in Northern Norway possesses favorable lime and potassium (K) fertilizer characteristics. However, enrichments of barium (Ba) and strontium (Sr) in carbonatite may cause an undesired uptake by plants when applied to agroecosystems. A field survey was carried out to compare concentrations of Ba, Sr, and macronutrients in indigenous plants growing in mineral soil developed on a bedrock of apatite–biotite–carbonatite (high in Ba and Sr) and of apatite–hornblende–pyroxenite (low in Ba and Sr) at Stjernøy. Samples of soil and vegetation were collected from three sites, two on carbonatite bedrock and one on pyroxenite bedrock. Ammonium lactate (AL)-extracted soil samples and nitric acid microwave-digested samples of soil, grasses, dwarf shrubs, and herbs were analyzed for element concentration using ICP-MS and ICP-OES. Concentrations of magnesium (Mg) and calcium (Ca) in both soil (AL) and plants were equal to or higher compared to values commonly reported. A high transfer of phosphorus (P) from soil to plants indicates that the apatite-P is available to plants, particularly in pyroxenite soil. The non-exchangeable K reservoir in the soil made a significant contribution to the elevated K transfer from soil to plant. Total concentrations of Ba and Sr in surface soil exhibited a high spatial variation ranging from 490 to 5,300 mg Ba kg^{-1} and from 320 to 1,300 mg Sr kg^{-1}. The transfer of AL-extractable elements from soil to plants increased in the order Ba < Sr < Ca < Mg < K, hence reflecting the chemical binding strength of these elements. Concentrations of Ba and Sr were low in grasses (≈ 20 mg kg^{-1}), intermediate in dwarf shrubs and highest in herbs. Plant species and their affinity for Ca seemed more important in explaining the uptake of Ba and Sr than the soil concentration of these elements. The leguminous plant species *Vicia cracca* acted as an accumulator of both Ba (1.800 mg kg^{-1}) and Sr (2.300 mg kg^{-1}).

Key words: apatite / carbonatite rock powder / fertilizer / transfer factor

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1 Introduction

Apatite–biotite–carbonatite rock from the Lillebukt Alkaline Complex at Stjernøy in Northern Norway (70°17.75' N, 22°34.5' E) shows favorable fertilizer and lime characteristics due to considerable amounts of various plant nutrients in minerals that weather quite easily. The nutrient potential of the rock is mirrored by rather lush vegetation in areas underlain by carbonatite rock (*Heim*, 2001). Compared to easily soluble commercial fertilizers, the carbonatite rock has the ability to remain in the soil for many years and slowly release its nutrients. This could be beneficial as the frequency of fertilization needed can be lowered (*Heim*, 2001; *Heim* et al., 2012) and the plant's demand for nutrients may be approached in a closer agreement compared to easily soluble mineral salts.

The main minerals are calcite (≈ 40 wt%), biotite (≈ 30 wt%), and apatite (≈ 7 wt%), in addition to some nepheline (*Gautneb*, 2009; *Heim* et al., 2012). Mineral separation can also provide concentrates of biotite (K, Mg) and apatite (P, Ca). Potassium, originating from the biotite and nepheline fraction of carbonatite rocks, is recovered in plants in significant amounts (*Bakken* et al., 1997; *Bakken* et al., 2000). The minerals in carbonatite rock are low in toxic and radiogenic metals such as cadmium (Cd), lead (Pb), uranium (U), and thorium (Th), but concurrent high concentrations of Ba and Sr have been observed up to 16.000 mg kg^{-1} and 8.600 mg kg^{-1}, respectively (*Heier*, 1961; *Gautneb*, 2009). In carbonatite rock, Ba primarily substitutes for K in the sheet interlayers of biotite due to their similar ionic radii (*Shaw* and *Penczak*, 1996; *Ibhi* and *Nachit*, 2000), and Sr substitutes for Ca in calcite; hence, they are released by the weathering of these minerals (*Heim* et al., 2012).

In its naturally occurring state, Sr has not been found to cause toxicity, unless at extremely high concentrations, and is therefore suggested to be of low concern (*ATSDR*, 2004). However, soluble Ba compounds can be highly toxic to biota

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(*Chaudhry* et al., 1977; *Llugany* et al., 2000; *Suwa* et al., 2008; *Kabata-Pendias*, 2010; *Melo* et al., 2011). No biological functions of Ba and Sr are reported in the literature; however, due to a similar biogeochemistry, plants may scarcely discriminate between certain elements such as Sr and Ca (*Kabata-Pendias*, 2010; *Marschner*, 2012). Plants with a high affinity for Ca may also accumulate Ba (*Myrvang* et al., 2016), but the knowledge of the biogeochemistry of Ba and Ba compounds in the soil–plant system is still relatively scarce.

Agrochemically, the carbonatite rock at Stjernøy consists of lime with an additional 2.6% K, 1.3% P, and 2.1% Mg. If plants were able to accumulate this element, an obstacle for its potential use in extensive agriculture would be the potential ecotoxicity of Ba when entering the food chain. Thus, the main objectives of the present study were to investigate concentrations of Ba in particular, but also of Sr, Ca, K, and Mg in soils and indigenous plants collected from three sites at Stjernøy. The availability of K, Mg, Ca, Ba, and Sr to plants was expected to be high, closely reflecting the soil mineralogy. In general, Ba and Sr were expected to be increased in plants in accordance with the acquisition of Ca.

2 Material and methods

Due to the heterogeneity of the carbonatite bedrock and for the sake of comparison, three sampling sites were chosen. Sites A and B are located on carbonatite bedrock high in Ba and Sr, whereas site C is located on apatite–hornblende–pyroxenite (AHP). Moreover, the latter is much poorer in these two elements (*Heim* et al., 2012). In August 2009, samples of vegetation and soil were collected from two comparable subsites of a size of 100–150 m^2 within each site (A1, A2, B1, B2, C1, and C2 in Fig. 1).

In total, 23 plant species with representatives of grasses, dwarf shrubs and herbs are presented in this work. Grasses and herbs were cut at the ground level, leaving the roots behind. Considering the dwarf shrubs, only the branches were sampled. Plant samples were stored for transportation in separate paper bags and dried at 60°C for 48 h. For most species, the dried material was divided into plant parts: leaf, stem, and flower/seed. Approximately 0.250 g accurately weighed samples of milled and sieved (2 mm) plant materials were microwave-digested (Milestone UltraClave 3) at 250°C (25 min at maximum temperature) with nitric acid (65 wt% HNO_3, sub-boiled ultrapure) prior to instrumental analysis. In addition to Ca, K, Mg, P, and sulfur (S), the concentrations of Ba and Sr were determined using ICP-MS (Perkin Elmer Siex Elan 6000) and ICP-OES (Perkin Elmer Optima 5300DV).

The mineral soil at Stjernøy mainly originates from the physical and chemical weathering of the bedrock after the last ice age. The soil is classified as a regolith with a soil depth of just a few decimeters on average and with no stratification and a low content of organic matter. From each site, approximately 2 kg of soil were sampled from the soil surface down to a maximum depth of 25 cm using a cylindrical auger (diameter of 2 cm). The bulk sample was mixed in a bucket and a subsample of 0.5 kg was stored in a plastic bag at approximately 4°C before analysis. Moist field soil was used to determine $pH_{(H_2O)}$ (1 : 2.5 soil–water suspension). The soil was dried (40°C) and sieved (2 mm) before determining the loss of ignition (LOI; 550°C). In addition, easily available plant P, K, Mg, and Ca were determined using Egnér's ammonium lactate (AL) method (*Egnér* et al., 1960; *Krogstad*, 1992). Roughly a tablespoon of the sieved soil was ground in a mortar and approximately 500 mg of accurately weighed soil were digested in 65 wt% $HNO_{3,}$ using the same procedure as for plant samples prior to the analysis of metal content using ICP-MS and ICP-OES. At site B, the K_{AL} and acid soluble K (1.0 M HNO_3 extraction) in crushed unweathered bedrock was also determined.

The quantification of elements using ICP-MS was consistent with measurements achieved using ICP-OES (R^2 ranged from 98 to 100%), thereby indicating a satisfactory removal of spectral interferences. Accuracy was checked by an analysis of standard reference materials: NCS (2004) DC 73350 leaves of poplar, NCS (2004) bush branch, IAEA (1985) hay powder v-10, NCS (2004) soil 73324, and NCS (2004) soil 7325. In general, the data were in agreement within a 95% confidence level or 2SD of the certified values issued. The repeatability (precision) of the method, based on three parallel samples of selected plant species and soil, was assessed to be of high quality (RSD < 5%).

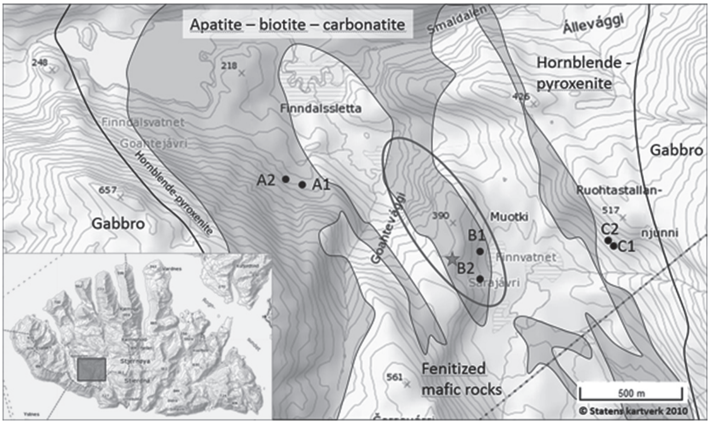

Figure 1: Soil and plant sampling sites A1-2, B1-2 and C1-2 at Lillebukt Alkaline Complex, Stjernøy, Northern Norway (70°17.75' N, 22°34.5' E). Circle represents area best suited for exploitation of carbonatite rock. Star marks area of mined bedrock.

The transfer of elements from soil to plant tissues was calculated using the transfer factor (TF):

$$TF = \frac{element\ in\ shoot\ tissue\ (mg\ kg^{-1})}{AL - element\ in\ soil\ (mg\ kg^{-1})}. \tag{1}$$

Non-parametric tests (*Velleman* and *Hoaglin*, 1984) were performed using the Excel XLSTAT 2016 software. Linear regression, analysis of variance (ANOVA) and Tukey's test, were also all performed using two different softwares, $R_{64x\ 3.2.2}$ and $R_{commander}$ (*Faraway*, 2002).

3 Results

3.1 Soil characteristics

The fraction of soil particles < 2 mm varied little among sampling sites (67–78 wt%; Table 1). The coarse fraction (> 2mm) at sites A and B consisted of 60 to 100% biotite besides calcite, while pyroxene and hornblende dominated at site C. Soil $pH_{(H2O)}$ was approximately neutral at site A (pH = 7.0, *n* = 4), moderately acidic at site B (pH = 5.8, *n* = 4), and acidic at site C (pH = 4.7, *n* = 4). The LOI demonstrated a narrow range of distribution with all sites close to 7%, except for the C-1 site reaching 11%. The highest total soil concentrations of Ba and Sr were found at site A and the lowest at site C (Table 1). Among the plant nutrients present in the 65 wt% HNO_3 extraction solution, K exhibited the highest relative spatial variability. At the two sites on carbonatite bedrock (A and B), the 65 wt% HNO_3-extractable K was three times higher compared to the soil on AHP rock (site C). Sulfur was the element that varied the least among sampling sites, with one exception, C-2, which had twice the concentrations compared to the others. Nitric acid-extractable P and Ca showed only small variations among sampling sites. At all locations, Ca_{AL} and Mg_{AL} were classified as high to very high relative to Norwegian standards for easily available plant nutrients in cultivated soils (*Krogstad*, 1992). The K_{AL} was low or average, with a large reservoir in the soil (Table 1). In unweathered bedrock at site B (marked with a star in Fig. 1), K_{AL} was 4.9 mg 100 g^{-1} and the 1 M HNO_3 soluble K was 600 mg 100 g^{-1}, with both estimates having a 20% measurement of uncertainty. Sampling site A-2 showed an increased concentration of Ca_{AL} compared to the others (Table 1). The P_{AL} varied more than P in the 65 wt% HNO_3 extraction solution and the availability to plants was classified as low at sites A and B and average at site C. The Ba_{AL} and Sr_{AL} were highest at site A-2, and lowest in the soil on AHP rock (site C).

3.2 Uptake of Ba, Sr, Ca, Mg, K, and P by plants

Median plant tissue concentrations (*n* = 2) of Ba and Sr in the 23 species investigated varied largely, ranging from roughly 12 to 1.800 mg Ba kg^{-1} and 10 to 2.300 mg Sr kg^{-1} (Tables 2 and 3). The lowest concentrations of Ba and Sr were observed in grasses and highest in herbs. Considering *V. cracca* in particular, exceptionally high concentrations of Ba (1.800 mg kg^{-1}) and Sr (2.300 mg kg^{-1}) were found (Tables 2 and 3), and this was the only leguminous species represented. For most of the plant species, Ba and Sr concentrations were lower than 500 and 900 mg kg^{-1}, respectively (Tables 2 and 3). Considering nutrients, median plant concentrations of Ca, Mg, and K ranged from 600 to 71.000 mg kg^{-1}, from 400 to 10.000 mg kg^{-1}, and from 3.300 to 61.000 mg kg^{-1}, respectively (Table 3). Figure 2 displays the notched box plots for leaves and stems of plant species common to all sampling subsites. The notches represent a 95% confidence interval of the median. The comparison of two groups or boxes whose notches intervals do not overlap can be considered significantly different (*Velleman* and *Hoaglin*, 1984; *Krzywinski* and *Altman*, 2014), and is, in the present work, used likewise by *Reimann* et al. (2001) to indicate differences in medians between sampling locations. Compared to sites A and B, a lower plant concentration of K and an elevated plant concentration of Mg and P were observed in species sampled at the site C (Fig. 2). The highest concentrations of Sr in plants were found at site A and the lowest at site C (Fig. 2). Considering the Ba and Ca concentrations in stems and leaves, only small differences between sampling sites were observed overall. Considering all grass species, however, the highest Ba concentrations were noticed at site B, while *V. cracca* closely reflected the bedrock chemistry with the highest Ba concentrations at site A and the lowest at site C (Table 2).

Considering Ba, Sr, Ca, Mg, and K, the highest median TF values were found for the stems and leaves of herbs, while the lowest median TF values, with the exception of K, were observed for grasses (Table 4). Considering all plant groups in general, the TFs increased in the order Ba < Sr < Ca < Mg < K.

A stepwise model selection was used to find models for the most optimal prediction of Ba and Sr uptake by plants related to sampling site and nutrient uptake. This model was based on 16 plant species common to all three sampling sites (Table 2), in which *V. cracca* was left out due to its extraordinary ability to accumulate Ba and Sr. Regarding three of the grass species (Table 2), leaves were not separated from the culm and, in the regression model, were defined as leaves. Except for *Euphrasia wettsteinii* and *Bartsia alpine*, of which flowers and leaves were combined, all plant species were divided into plant parts (*i.e.*, leaf and stem; Table 2). Considering the different macronutrients, Ca gave the best correlation to Ba uptake in plants at all sampling sites (Fig. 3, $P < 0.1\%$). When comparing Ba and Sr concentrations of stems relative to leaves, only the 11 plant species that were divided into stems and leaves, and common to all sampling sites, were included in the regression model. In one way or another, Ba concentrations varied between plant parts. Nonetheless, when comparing the different species of grasses, dwarf shrubs, and herbs, no significant trends in tissue Ba accumulation were revealed (Tukey's test: $P > 10\%$). The plant uptake of Sr was closely related to Ca uptake at all sampling sites ($P < 0.1\%$; Fig. 3), with the highest uptake by leaves compared to stems (Tukey's test: $P < 0.1\%$).

4 Discussion

4.1 Availability of Ba, Sr, Ca, Mg, K, and P in soil and transfer to plants

The soil at sites A and B in this study contained Ba concentrations above the agricultural soil-quality limits suggested by the Canadian Soil Quality Guidelines (*CCME*, 2013), as well as above the concentrations reported to induce a significant reduction in the yield of bush bean (*Chaudhry* et al., 1977). However, considering the source of Ba and its influence on

Table 1: Selected soil characteristics, median and range (n = 4) of barium (Ba), strontium (Sr), calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), and sulfur (S) at each sampling site (A, B, C) at Stjernøy (see map in Fig. 1). All element concentrations are given in mg kg^{-1}.[a]

	A-1		**A-2**		**B-1**		**B-2**		**C-1**		**C-2**	
	Median	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
pH	6.8a	6.8–6.9	7.2a	7.2–7.3	5.6a	5.5–5.8	6.0a	5.9–6.0	4.7a	4.6–4.7	4.7a	4.7–4.8
LOI / %	8.3	7.6–8.9	6.7	5.7–7.0	7.3	6.6–28.3	7.4	6.7–15.1	11.6	10.4–12.2	5.9	4.5–7.4
PS < 2mm / %	77.8a	77.5–78.0	77.1a	76.1–78.1	74.9a	73.8–76.0	76.0a	74.9–77.1	67.2a	66.6–67.8	68.9a	67.5–70.4
	65 wt% HNO_3 soluble element											
Ba_{soil}	5630	4770–5930	4500a	3750–5260	1800	1690–1880	1220a	1215–1230	573a	549–597	486a	477–496
Sr_{soil}	1030	972–1360	1350a	993–1701	918	886–985	1180a	1110–1260	472a	471–472	419a	405–433
Ca_{soil}	38000	35600–55400	52900a	36800–69100	51200	48600–53800	71200a	67400–75000	68360a	68340–68380	65100a	63100–67200
Mg_{soil}	23500	22600–24800	21000a	20600–21400	19900	19500–20400	21600a	21100–22000	33800a	32400–35200	31900a	30300–33500
K_{soil}	31100	26700–32700	25700a	22800–28600	16700	16200–18300	16100a	15800–16500	9610a	9170–10000	8290a	8070–8500
P_{soil}	1930	1460–2230	1960a	1880–2050	1430	1320–1450	2400a	2200–2590	2590a	1760–3400	2090a	1990–2200
S_{soil}	230	226–243	261a	261–262	187	183–194	235a	212–258	448a	428–468	227a	220–234
	0.1 M ammonium lactate (AL) soluble element											
Ba_{AL}	150	140–155	323	316–332	230	203–233	246	239–251	24.1	23.2–26.0	17.9	15.1–20.0
Sr_{AL}	125	116–136	458	371–587	85.0	69.6–95.4	101	98.5–102	17.4	16.4–19.4	12.2	9.93–14.1
Ca_{AL}	3180	2970–3560	14800	11400–18600	2690	2240–3050	4040	3950–4110	1070	968–1210	758	584–905
Mg_{AL}	117	110–130	184	162–208	189	172–201	141	132–150	165	158–201	128	94.4–167
K_{AL}	80.0	69.7–86.7	33.6	29.1–37.4	51.5	50.8–59.0	37.2	33.2–38.0	84.9	82.2–104	53.8	49.9–61.5
P_{AL}	3.48	2.93–3.92	6.85	5.82–7.26	11.4	9.59–12.1	8.73	8.49–11.3	35.5	34.4–37.8	42.0	35.8–49.5
S_{AL}	–	–	–	–	–	–	–	–	–	–	–	–

[a] LOI: loss of ignition. PS: particle size. a: the number of samples (n = 2).

Table 2: Median barium (Ba) concentrations (mg kg^{-1}, $n = 2$) of plants collected at sampling sites A, B, and C at Stjernøy (see map in Fig. 1).[a]

Plant species	**Ba**								
	A			**B**			**C**		
	Leaves	**Stems**	**Flowers**	**Leaves**	**Stems**	**Flowers**	**Leaves**	**Stems**	**Flowers**
Grasses									
Poa pratensis L. (Common meadow grass)	29b	–	–	29b	–	–	25b	–	–
Phleum alpinum L. (Alpine timothy)	26b	–	–	28b	–	–	21b	–	–
Anthoxanthum odoratum L. (Sweet vernal grass)	37b	–	–	55b	–	–	26b	–	–
Deschampsia cespitosa (L.) P. Beauv. (Tufted hair grass)	45	23	–	47	25	–	36	19	–
Calamagrostis phragmitoides Hartm. (Small reed)	–	–	–	56c	14c	–	37	12	–
Shrubs									
Vaccinium myrtillus L. (Blueberry)	78c	130c	–	–	–	–	84	140	–
Salix sp. L. (Willow)	93	140	–	120	140	–	82	76	30
Salix reticulata L. (Netleaf willow)	100	110	–	140	130	–	–	–	–
Herbs									
Ranunculus acris L. (Meadow buttercup)	310	340	21	230	220	68	180	210	30
Rumex acetosa L. (Sorrel)	140	78	15	170	89	23	150	57	19
Alchemilla alpina L. (Alpine ladyl's mantle)	–	–	–	110	180	90	73	130	43
Saussurea alpina (L.) DC. (Alpine saw-wort)	310	270	87	200c	180	53	200	240	48
Euphrasia wettsteinii Gussarova (Mountain eyebright)	160ac	220c	–	180a	280	–	150ac	190	–
Solidago virgaurea L. (Goldenrod)	120	180	–	190	170	–	120	150	–
Saxifraga aizoides L. (Saxifrage)	120	120	84	130	150	86	–	–	–
Angelica archangelica L. (Wild celery)	140	130	110	170	300	88	140	190	58
Taraxacum sp. (Dandelion)	150	–	–	160	–	–	190	–	–
Alchemilla sp. L. (Ladyl's mantle)	220c	420c	310c	340	390	290	200	230	140c
Silene dioica (L.) Clairv. (Red campion)	160	85	–	150	62	–	100	96	–
Equisetum sp. L. (Horsetail)	160b	–	–	290b	–	–	180b	–	–
Bartsia alpina L. (Velvetbells)	150a	260	–	194a	340	–	71a	190	–
Silene acaulis (L.) J. (Moss campion)	820c	–	200c	600c	–	30c	–	–	–
Vicia cracca L. (Bird vetch)	1800	940	370	860	440	200	290	130	58

[a] –: no data. a: leaf and flower combined; b: whole plant except roots; c: the number of samples ($n = 1$).

Table 3a: Median concentrations (mg kg^{-1}, $n = 2$) of strontium (Sr) and calcium (Ca) of plants collected at sampling sites A, B, and C at Stjernøy (see map in Fig. 1). [a]

Plant species	**Sr**						**Ca**					
	A		**B**		**C**		**A**		**B**		**C**	
	Leaves	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**
Grasses												
P. pratensis L.	70b	–	40b	–	30b	–	2200b	–	1600b	–	2000b	–
P. alpinum L.	40b	–	30b	–	20b	–	1200b	–	1300b	–	1400b	–
A. odoratum L.	50b	–	50b	–	20b	–	2000b	–	2300b	–	1400b	–
D. cespitosa L.	70	40	50	30	30	20	2400	1200	2200	1000	2200	1100
C. phragmitoides L.	–	–	60	20	–	10	–	–	3100	610	–	630
Shrubs												
V. myrtillus L.	120c	90	–	–	40	40	5700c	3100	–	–	7600	4500
Salix sp. L.	340	180	370	170	240	100	9900	5100	14000	6200	16000	5800
S. reticulata L.	640	190	650	230	–	–	19000	5700	23000	8100	–	–
Herbs												
R. acris L.	860	290	540	210	280	130	30000	7800	24000	7200	21000	6800
R. acetosa L.	370	160	280	120	230	80	16000	3800	15000	3400	20000	3500
A. alpina L.	–	–	250	280	110	130	–	–	10000	9400	9200	7500
S. alpine L.	690	260	550	220	240	110	25000	6600	26000	6900	19000	6200
E. wettsteinii G.	460a	330	360a	300	180a	90	14000a	7900	15000a	10000	13000a	5100
S. virgaurea L.	470	210	490	170	210	90	18000	5500	22000	5200	18000	4900
S. aizoides L.	850	560	600	340	–	–	28000	14000	24000	11000	–	–
A. archangelica L.	720	350	530	470	330	240	27000	8300	24000	14000	25000	12000
Taraxacum sp. L.	540	–	440	–	260	–	16000	–	19000	–	19000	–
Alchemilla sp. L.	440	380a	420	360	290	250	14000	9500a	18000	12000	20000	13000
S. dioica L.	440	130	360	120	170	90	15000	2900	14000	3300	12000	3900
Equisetum sp. L.	760b	–	590b	–	310b	–	24b	–	25b	–	22b	–
B. alpina L.	510a	170	510a	170	170a	100	16000a	3900	20000a	4400	11000a	4300
S. acaulis L.	400c	–	640c	–	–	–	39000c	–	25c	–	–	–
V. cracca L.	2300	1000	930	330	460	210	71000	24000	41000	11000	33000	11000

[a] –: no data. a: leaf and flower combined. b: whole plant except roots. c: the number of samples ($n = 1$).

Table 3b: Median concentrations (mg kg^{-1}, n=2) of magnesium (Mg) and potassium (K) of plants collected at sampling sites A, B and C at Stjernøy (see map in Fig. 1).

Plant species	**Mg**						**K**					
	A		**B**		**C**		**A**		**B**		**C**	
	Leaves	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**	**Leaves**	**Stems**
Grasses												
P. pratensis L.	520b	–	440b	–	700b	–	12000b	–	11000b	–	12000b	–
P. alpinum L.	530b	–	700b	–	900b	–	13000b	–	12000b	–	12000b	–
A. odoratum L.	610b	–	600b	–	800b	–	14000b	–	14000b	–	12000b	–
D. cespitosa L.	830	660	900	700	1400	920	14000	15000	17000	16000	11000	14000
C. phragmitoides L.	–	–	1000	410	–	500	–	–	16000	7900	–	7200
Shrubs												
V. myrtillus L.	2100c	1000	–	–	2600	1100	7600c	4000	–	–	7000	3500
Salix sp. L.	1800	1100	2400	880	3800	1400	14000	4800	12000	4700	9100	6100
S. reticulata L.	2000	560	2100	1000	–	–	17000	4100	14000	6600	–	–
Herbs												
R. acris L.	2800	1700	2000	1100	3700	2100	36000	36000	28000	29000	15000	21000
R. acetosa L.	3900	1700	4000	1400	8000	2600	34000	23000	36000	32000	22000	16000
A. alpina L.	–	–	1700	1600	3300	2400	–	–	12000	18000	9400	14000
S. alpine L.	4800	2000	3500	1600	9500	4800	52000	40000	44000	30000	38000	25000
E. wettsteinii G.	3300a	1600	3100a	1500	6500a	2300	43000a	41000	34000a	35000	27000a	34000
S. virgaurea L.	2300	1000	2800	1000	7200	2600	37000	25000	38000	25000	23000	14000
S. aizoides L.	2500	2000	2700	1900	–	–	18000	26000	17000	22000	–	–
A. archangelica L.	2600	1200	1900	1600	3400	2800	38000	40000	36000	49000	25000	26000
Taraxacum sp. L.	2100	–	3300	–	8300	–	55000	–	50000	–	31000	–
Alchemilla sp. L.	3800	3000a	4100	2500	4700	2600	21000	24000a	21000	26000	13000	14000
S. dioica L.	2200	860	3200	1200	3900	2700	61000	39000	48000	33000	50000	42000
Equisetum sp. L.	3000b	–	2300b	–	4800b	–	24000b	–	26000b	–	21000b	–
B. alpina L.	2600a	750	2200a	820	2700a	1500	29000a	18000	28000a	19000	17000a	18000
S. acaulis L.	2500c	–	2200c	–	–	–	23000c	–	35000c	–	–	–
V. cracca L.	2700	3100	4500	3000	3500	4300	15000	20000	16000	20000	11000	10000

[a]–: no data. a: leaf and flower combined. b: whole plant except roots. c: the number of samples ($n = 1$).

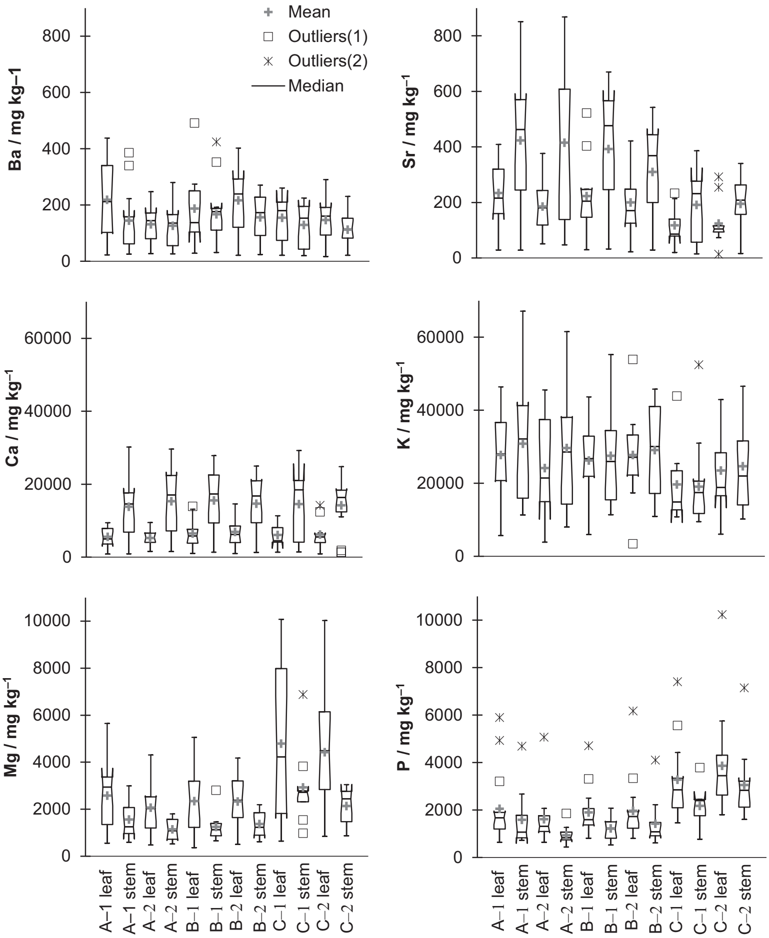

Figure 2: Notched box plot showing median, interquartile range (IQR, representing 50% of the data), and whiskers (including 99% of the data) for Ba, Sr, Ca, K, Mg, and P in leaves/shoots and stems of plants common to all sampling sites (A, B, and C). Outlier (1): > 1.5 × IQR. Outlier (2): > 3 × IQR.

plant Ba uptake, the element's chemical characteristics are decisive for its availability. The total metal content of soil includes fractions that are not readily available to plants (*Zhang* et al., 2001). Hence, in order to determine the availability, accessibility, and mobility of elements, the biologically active fraction is of more interest than the total content (*Cottenie* et al., 1980). The AL-extractable element concentration may be an estimate of an exchangeable fraction in soil, which reflects the availability to plants (*Øgaard* et al., 2002). Despite large variations in concentrations of Ba in both soil and plants, the actual uptake was generally a poor reflection of the soil chemistry of the respective sites. Barium is immobilized at increased pH (*Kabata-Pendias*, 2010; *Madejón*, 2013); thus, differences in soil pH (Table 1) may partly explain why the majority of plant species did not accumulate more Ba at site A compared to site B (Table 2). Depending on the organic content of the soil, the availability of certain plant nutrients such as Ca, Mg, and K in alkaline-calcareous soils (pH > 7.0) may be relatively high compared to soils with a low pH (*McKenzie*, 2003; *Brady* and *Weil*, 2004). The highest concentration of nitric acid-extractable Ca was measured at site C, yet the exchangeable Ca fraction was still the lowest (Table 1). This is likely due to the soil mineralogy with Ca in soil bound to the silicates pyroxene and hornblende (site C) compared to easily soluble Ca-carbonate in the carbonatite (sites A and B). High plant K : Mg ratios at sites A and B (Table 3) may be explained by an antagonistic relationship between these two elements, in which a high K uptake by plants depresses the uptake of Mg (*Jefferson* et al., 2001; *Yara*, 2015). On the contrary, at site C high plant Mg : K ratios were observed (Table 3), hence reflecting the soil's mineralogy, exhibiting the lowest total K and the highest total Mg at site C (Table 1).

In general, concentrations of Ba, Sr, Ca, K, P, and Mg of the plants collected at Stjernøy were in accordance with or higher compared with concentrations observed in the northern parts of Europe (*Reimann* et al., 2001; *Gjengedal* et al., 2015). The high variability in the transfer of elements from soil to plants is

Table 4: Element transfer factors (TF) from soil to plant for 23 plant species collected at sampling sites A, B and C at Stjernøy (see map in Fig. 1).

Element		**Grasses**	**Dwarf shrubs**		**Herbs**		
		Shoots	**Leaves**	**Stems**	**Leaves**	**Stems**	**Flowers**
Ba	Range	0.065–2.1	0.35–8.6	0.43–7.0	0.40–17	0.24–16	0.023–5.8
	Median	0.60	0.94	1.1	1.28	1.1	0.80
Sr	Range	0.10–2.66	0.57–23.6	0.42–9.5	0.83–39.5	0.22–23.9	0.040–14
	Median	1.2	3.7	2.8	4.0	3.3	2.6
Ca	Range	0.10–3.6	0.58–24	0.40–8.9	0.75–45	0.17–19	0.19–17
	Median	1.29	4.3	2.9	4.5	3.4	3.2
Mg	Range	1.9–10.9	7.4–27.6	3.3–15.6	7.1–77.6	2.8–39.8	2.6–37.3
	Median	6.7	15	8.9	16	14	14
P[a]	Range	41–346	84–588	121–325	71–1700	21–1360	n.d
	Median	120	170	186	168	128	n.d
K	Range	72–490	43–501	38–163	85–1800	115–1500	41–911
	Median	260	260	120	380	380	320

[a] Dataset for phosphorus includes leaves and stems of 16 species common to all sampling sites only.

related to both binding strengths of elements to soil (mineral), the biogeochemical differences among plant species and their acquisition of certain nutrients over others (*NORSØK*, 2003; *Gjengedal* et al., 2015). Other factors related to availability of nutrients to plants comprise, *e.g.*, pH, soil organic matter, cation exchange capacity, microbial activity, and rhizosphere activity. In our study, there is a pool of potential interacting factors that influence the availability of nutrients. Besides the AL-extractable elements in carbonatite and pyroxenite, the availability of nutrients can also be estimated by the transfer factors given in Table 4.

It is remarkable in Table 4 that the TF values of elements for all plant groups reflect the binding strength of ions to soil in the increasing order of K < Mg < Ca < Sr < Ba. Despite significantly higher Ba_{AL} and Sr_{AL} compared to K_{AL} and Mg_{AL}, the relatively moderate concentrations of Ba and Sr in plants indicate a rather low acquisition potential by plants and a high retention in soil. The exception to this is the leguminous species *Vicia cracca*. This species had a TF of 17, which indicates a specific ability to acquire additional Ba and Sr from non-exchangeable reserves in soil. In contradiction to the high plant K concentrations observed at all sampling sites, only low K_{AL} was noticed. This is explained by the high potential of plants to acquire this easily available element from both exchangeable and non-exchangeable sites due to, *e.g.*, rhizosphere interaction, followed by the replenishment of K from interlayer and structural K in soil (*Jungk* and *Claassen*, 1986; *Marschner*, 1995; *Jungk*, 2001; *Øgaard* et al., 2002; *Øgaard* and *Krogstad*, 2005). Accordingly, calculations based on a correction between the K_{AL} (4.9 mg 100 g^{-1}) and 1 M HNO_3-soluble K concentration (600 mg 100 g^{-1}; values based on measurements of mined rock at site B) is probably a closer estimate for the true plant-available K fraction in carbonatite. The estimated available K (*NIBIO*, 2009; *Yara*, 2015) can be calculated as follows:

$$\text{Plant-available K (mg 100 g}^{-1}\text{)} = (600 - 4.9) \times 0.15, \qquad (2)$$

which roughly corresponds to 900 kg K ha^{-1}, a reserve considered very high from an agrochemical point of view (*Krogstad*, 1992). Looking upon the TF values for K, this correction provides a more meaningful explanation for the high K uptake by plants. In the same way as for K, the high transfer of P and Mg may also indicate that the plants acquire these nutrients from both the P_{AL} and Mg_{AL}-soluble soil fraction as well as from soil reserves.

4.2 Plant uptake of Ba and Sr compared to Ca

As derived from the regression analyses, the plant species and their affinity for Ca were much more important in explaining both Ba and Sr uptake, rather than the soil concentrations of these elements. The close correlation between Sr and Ca in plants was expected because of their geochemical relationship in the soil minerals (calcite at sites A and B, pyroxene and hornblende at site C). Strontium is absorbed corresponding to the plant's metabolic requirements for Ca (*Kabata-Pendias*, 2010). On the other hand, the relationship of Ba to Ca has been indicated in a few case studies. The results of this work suggest that the plant's acquisition for Ca seems to also enhance its uptake of Ba, supporting findings by *Myrvang* et al. (2016) and indications proposed by *Wallace* and *Romney* (1971). This may be an effect of the plant's poor ability to discriminate between alkaline earth metals with a similar geo-

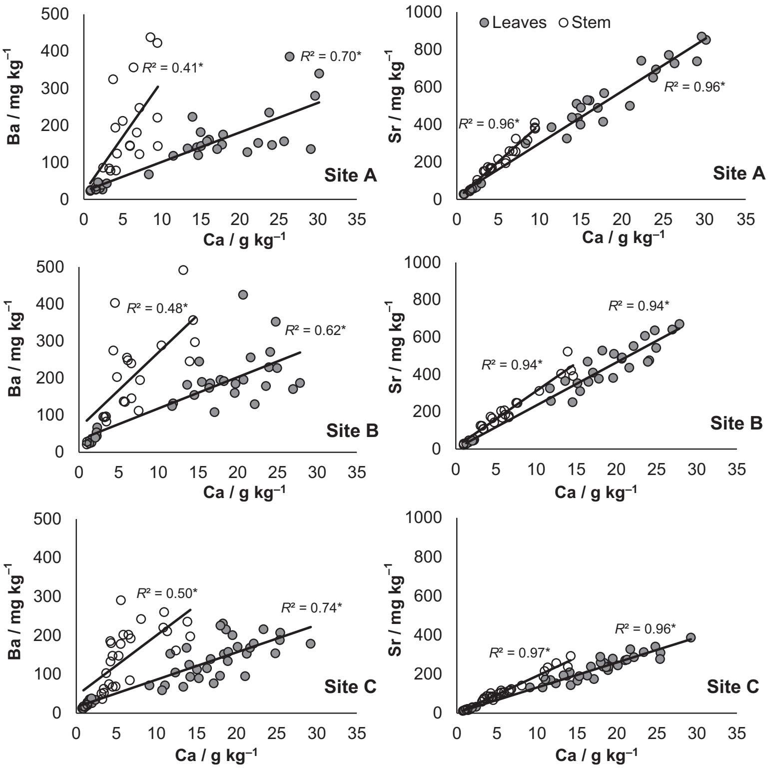

Figure 3: Concentrations of strontium (Sr) and barium (Ba) relative to calcium in leaves/shoots of 16 plant species, and associated stems of 11 of these plants, collected at sampling sites A, B, and C. *Vicia cracca* is not included in the analyzed data matrix. Asterisks represent significance within a 95% confidence level.

chemistry (*Marschner*, 2012). Interactions between the alkaline earth metals are complex and although they can compete with each other, Ba and Sr cannot replace Ca in biochemical functions. *Kabata-Pendias* (2010) indicates a highly variable distribution of Sr in plants but reports no information on Ba distribution. Depending on several soil and plant factors, an increased level of Ca in growth media may both inhibit and stimulate Sr uptake (*Kabata-Pendias*, 2010) and Ba uptake (*Myrvang* et al., 2016) by plants. A pot experiment, investigating the treatment effect of lime ($CaCO_3$) on uptake and the interspecies distribution of Ba, revealed a complex relationship between the antagonistic effect of Ca on Ba transfer from soil to roots, as well as the distribution of these two elements within plants (*Myrvang* et al., 2016). The present work demonstrates that compared to Sr the similarity of the distribution of Ba between plant parts is more pronounced, as shown by a lower Ba : Ca ratio in stems compared to leaves (Fig. 2).

Considering the future possibilities for the agricultural use of carbonatite rock powder, the low uptake of Ba by grasses is advantageous. The high potential for Ba accumulation by *V. cracca*, however, may be a cause of concern. *V. cracca* was not considered in the regression analyses because the tissue concentrations of Ba, Sr, and Ca were highly elevated compared to all the other species. If *V. cracca* had been included in the model it would have masked the differences between the other species. With *V. cracca* being the only species representing legumes, it is not possible to assess whether the high Ba and Sr concentrations indicate a general trend for legumes grown on carbonatite soil. Nevertheless, *Myrvang* et al. (2016) found *V. cracca* to accumulate Ba from a tectosilicate soil (with Ba primarily substituting K in feldspars) in significantly higher amounts compared to other legumes, vegetables and grasses, thereby supporting our findings of this particular species being an accumulator of Ba.

Compared to grasses, the higher transfer of Ba and Sr to herbs in general is proposed to relate to a higher affinity for Ca. To the best of our knowledge, the literature covering the link between Ba and Ca in herbs compared to grasses is rather limited. Compared to grasses and cereals, a high affinity for Ca by legumes and herbs is reported in the literature (*e.g.*, *Loneragan* and *Snowball*, 1969), while similar trends for Ba were suggested by *Robinson* et al. (1950), though without considering the interaction of these two elements within plants. In the presence of Ca, the Ba uptake to roots is suggested to be limited due to the antagonistic interactions of Ca and Ba during uptake by roots (*Wallace* and *Romney*, 1971). The transfer of Ba to plants in general was rather limited, which could potentially be related to the high presence of Ca in soil. However, *Myrvang* et al. (2016) suggested that plants with a high demand for Ca were less affected by the potential antagonistic effect of Ca on Ba uptake, which is also reflected in *V. cracca*. Plant-dependent differences as well as the influence of microbial activity probably contributed to the large variations in the uptake of Ba, Sr, Ca, Mg, and K (*Cipollini* and *Pickering*, 1986; *Løes* et al., 1998; *Aerts* and *Chapin*, 1999; *Marschner*, 2012). Differences in yield also probably contribute to the variation in the concentration of Ba and other elements among plant species. Due to a potential dilution effect, the total plant uptake of elements, as compared to the concentration to plants, may give quite a different picture of a plant's potential to acquire elements from a soil medium (*Myrvang* et al., 2016). Since the whole plant dry weight was not measured in this survey, the dilution effects could not be determined.

5 Conclusions

Compared with the background levels of major elements determined in native plant species growing in the northern parts of Europe, tissue concentrations of Ca, Mg, P, and K in indigenous plants at Stjernøy were equally high or higher, thus, suggesting a high nutrient availability to plants. The concentrations of Sr and K of plants grown in soil on AHP bedrock were lower compared to those grown in soil on carbonatite bedrock, with an opposite trend for Mg and P, hence reflecting the soil mineralogy. In general, the transfer of Ba and Sr from soil to plants was somewhat limited compared to the transfer of K, Mg, and Ca, which might reflect the retention potential of Ba and Sr in soil. Nonetheless, as for Sr, the variation in the concentration of Ba in plant tissues seems to be mostly affected by the species-dependent requirements for Ca, rather than for the soil concentrations of these elements. Grasses had the lowest concentration of Ba ($\approx$ 30 mg kg^{-1}) and Sr ($\approx$ 60 mg kg^{-1}), which is advantageous regarding the potential use of carbonatite rock powder as a fertilizer or soil amendment. Herbs had a higher Ba and Sr concentrations compared to grasses and dwarf shrubs. Moreover, the leguminous species *V. cracca* acted as an accumulator of Ba and Sr, with its exceptionally high tissue concentrations reaching 2.000 mg Ba kg^{-1} and 2.300 mg Sr kg^{-1}. Further investigations on the mechanisms influencing Ba and Sr availability and the uptake from carbonatite rock powder are in progress.

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References

Aerts, R., *Chapin, F. S.* (1999): The mineral nutrition of wild plants revisited: A re-evaluation of processes and patterns. *Adv. Ecol. Research.* 30, 1–67.

ATSDR—Agency of Toxic Substances and Disease Registry (2004): Public Health Statement for Strontium. Agency for Toxic Substances & Disease Registry, Atlanta, GA, USA. Available at: http://www.atsdr.cdc.gov/phs/phs.asp?id=654&tid=120.

Bakken, A. K., *Gautneb, H.*, *Myhr, K.* (1997): The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. *Nutr. Cycl. Agroecosyst.* 47, 41–48.

Bakken, A. K., *Gautneb, H.*, *Sveistrup, T.*, *Myhr, K.* (2000): Crushed rocks and mine tailings applied as K fertilizers on grassland. *Nutr. Cycl. Agroecosyst.* 56, 53–57.

Brady, N. C., *Weil, R. R.* (2004): Element of the Nature and Properties of Soils. 2nd Ed. Pearson Education Ltd., Harlow, UK.

CCME (2013): Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Barium. Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada. Available at: http://ceqg-rcqe.ccme.ca/download/en/258.

Chaudhry, F. M., *Wallace, A.*, *Mueller, R. T.* (1977): Barium toxicity in plants. *Commun. Soil Sci. Plan.* 8, 795–797.

Cipollini, M. L., *Pickering, J. L.* (1986): Determination of the phytotoxicity of barium in leach-field disposal of gas-well brines. *Plant Soil* 92, 159–169.

Cottenie, A., *Camerlynck, R.*, *Verloo, M.*, *Dhaese, A.* (1980): Fractionation and determination of trace elements in plants, soils and sediments. *Pure Appl. Chem.* 52, 45–53.

Egnér, H., *Riehm, H.*, *Domingo, W. R.* (1960): Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor- und Kaliumbestimmung. *Kungliga Lantbrukshögskolans annaler* 26, 199–215.

Faraway, J. J. (2002): Practical regression and ANOVA using R. Available at: https://cran.r-project.org/doc/contrib/Faraway-PRA.pdf.

Gautneb, H. (2009): Review of the geology and the apatite distribution of the carbonatite in the Lillebukt Alkaline Complex, Stjernøy Northern Norway. *Geological Survey of Norway Report* 2009.061, 1–33.

Gjengedal, E., *Martinsen, T.*, *Steinnes, E.* (2015): Background levels of some major, trace, and rare earth elements in indigenous plant species growing in Norway and the influence of soil acidification, soil parent material, and seasonal variation on these levels. *Environ. Monitor. Assess.* 187, 386–414.

Heier, K. S. (1961): Layered gabbro, hornblendite, carbonatite and nepheline syenite on Stjernøy, North Norway. *Norsk Geol. Tidskr.* 41, 109–155.

Heim, M. (2001): Norsk steinmel til (øko-)landbruk: Historikk, status quo, utfordringer og muligheter. Nordisk Mineralsymposium 2000, Verdiskapning fra mineral til ferdig produkt. Trondheim, Norway, pp. 16–21.

Heim, M., *Hillersøy, M. H.*, *Bleken, M. A.*, *Gautneb, H.*, *Gjengedal, E. L.* (2012): Apatite-biotite-carbonatite (Stjernøy, N-Norway) – potential and obstacles regarding a multi nutrient rock-fertilizer. Proceedings of the 10th International Congress for Applied Mineralogy (ICAM). Springer eBooks, pp. 327–334.

Ibhi, A., *Nachit, H.* (2000): The substitution mechanism of Ba and Ti into phyllosilicate phases: the example of barium-titanium biotite. *Ann. Chimie Sci. Matériaux* 25, 627–634.

Jefferson, P. G., *Mayland, H. F.*, *Asay, K. H.*, *Berdahl, J. D.* (2001): Plant genetic resources variation in mineral concentration and grass tetany potential among Russian wildrye accessions. *Crop Sci.* 41, 543–548.

Jungk, A., *Claassen, N.* (1986): Availability of phosphate and potassium as the result of interactions between root and soil in the rhizosphere. *J. Plant Nutr. Soil Sci.* 149, 411–427.

Jungk, A. (2001): Root hairs and the acquisition of plant nutrients from soil. *J. Plant Nutr. Soil Sci.* 164, 121–129.

Kabata-Pendias, A. (2010): Trace Elements in Soils and Plants. 4th Ed. CRC Press, Boca Raton, FL, USA.

Krogstad, T. (1992): Methods for Soil Analysis. Report no. 6/92. Institute of Soil Science, Norwegian Agricultural College, Ås, Norway (in Norwegian).

Krzywinski, M., *Altman, N.* (2014): Points of significance: Visualizing samples with box plots. *Nature Meth.* 11, 119–120.

Llugany, M., *Poschenrieder, C.*, *Barceló, J.* (2000): Assessment of barium toxicity in bush beans. *Arch. Environ. Con. Tox.* 39, 440–444.

Loneragan, J. F., *Snowball, K.* (1969): Calcium requirements of plants. *Aust. J. Agric. Res.* 20, 465–477.

Løes, A. K., *Øgaard, A. F.* (1998): Changes in the nutrient content of agricultural soil on conversion to organic farming in relation to farm-level nutrient balances and soil contents of clay and organic matter. *Acta Agric. Scand. B-S. P.* 47, 201–214.

Madejón, P. (2013): Barium, in Alloway, B. J. (ed.): Heavy Metals in Soils—Trace Metals and Metalloids in Soils and their Bioavailability, 3rd Ed. Springer, Heidelberg, Germany, pp. 507–513.

Marschner, H. (1995): Mineral Nutrition of Higher Plants. 2nd Edition. Academic Press, London, UK.

Marschner, P. (2012): Mineral Nutrition of Higher Plants. 3rd Edition. Academic Press, London, UK.

McKenzie, R. H. (2003): Soil pH and Plant Nutrients. AGRI-FACTS. Alberta Agriculture, Food and Rural Development, Edmonton, AB, Canada.

Melo, L. C. A., *Alleoni, L. R. F.*, *Carvalho, G.*, *Azevedo, R. A.* (2011): Cadmium- and barium-toxicity effects on growth and antioxidant capacity of soybean (*Glycine max* L.) plants, grown in two soil types with different physicochemical properties. *J. Plant Nutr. Soil Sci.* 174, 847–859.

Myrvang, M. B., *Bleken, M. A.*, *Krogstad, T.*, *Heim, M.*, *Gjengedal, E.* (2016): Can liming reduce barium uptake by agricultural plants grown on sandy soil? *J. Plant Nutr. Soil Sci.* 179, 557–565.

NIBIO (2009): Fertilizer Handbook. *Norwegian Institute of Bioeconomy Research*, Ås, Norway. Available at: www.bioforsk.no/gjodslingshandbok.

NORSØK (2003): Økologisk Handbok—Jordkultur og Næringstilgang. GAN Forlag AS, Oslo, Norway.

Øgaard, A. F., *Krogstad, T.*, *Lunnan, T.* (2002): Ability of some Norwegian soils to supply grass with potassium (K) – soil analyses as predictors of K supply from soil. *Soil Use and Manage.* 18, 412–420.

Øgaard, A. F., *Krogstad, T.* (2005): Release of interlayer potassium in Norwegian grassland soils. *J. Plant Nutr. Soil Sci.* 168, 80–88.

Reimann, C., *Koller, F.*, *Frengstad, B.*, *Kashulina, G.*, *Niskavaara, H.*, *Englmaier, P.* (2001): Comparison of the element composition in several plant species and their substrate from a 1 500 000-km^2 area in Northern Europe. *Sci. Tot. Environ.* 278, 87–112.

Robinson, W. O., *Whetstone, R. R.*, *Ergington, G.* (1950): The occurrence of barium in soils and plants. *U.S. Dept. Agric. Tech. Bull.* 1013, 1–36.

Shaw, C. S. J., *Penczak, R. S.* (1996): Barium- and titanium-rich biotite and phlogopite from the western and eastern gabbro, Coldwell alkaline complex, northwestern Ontario. *Can. Mineral.* 34, 967–975.

Suwa, R., *Jayachandran, K.*, *Nguyen, N. T.*, *Boulenouar, A.*, *Fujita, K.*, *Saneoka, H.* (2008): Barium toxicity effects in soybean plants. *Arch. Environ. Con. Tox.* 55, 397–403.

Velleman, P. F., *Hoaglin, D. C.* (1984): Applications, Basics, and Computing of Exploratory Data Analysis. Duxbury Press, Boston, MA, USA.

Wallace, A., *Romney, E. M.* (1971): Some interactions of Ca, Sr and Ba in plants. *Agron. J.* 63, 245–248.

Yara (2015): Fertilizer Handbook 2014/2015. Yara Norway AS. Oslo, Norway. Available at: https://yaraurl.com/hnd0 (in Norwegian).

Zhang, H., *Zhao, F.-J.*, *Sun, B.*, *Davison, W.*, *McGrath, S. P.* (2001): A new method to measure effective soil solution concentration predicts copper availability to plants. *Environ. Sci. Technol.* 35, 2602–2607.

Paper II

Can liming reduce barium uptake by agricultural plants grown on sandy soil?

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Abstract

Uptake of barium (Ba) from soil by vascular plants varies among species. Despite the toxicity of soluble Ba compounds to plants, research on mechanisms controlling Ba uptake from natural soils is scarce. This study investigated the treatment effect of lime ($CaCO_3$) added to a sandy soil containing a total of 500 mg Ba kg^{-1} on uptake and interspecies distribution of Ba in legumes and other cultivated food and feed plants. Nine species of grasses, vegetables, herbs, and legumes were cultivated under controlled conditions in a greenhouse experiment. The plants were harvested at maturity or flowering, dried, milled, and digested with nitric acid using the microwave technique prior to ICP-MS analysis. All plant species acquired Ba from the soil in considerable amounts, probably due to low Ba adsorption potential of the sandy soil. Shoot tissue concentrations ranged from about 100 (grass) to 600 mg Ba kg^{-1} (legume) and root concentrations from about 100 (tuber vegetable) to 700 mg kg^{-1} (legume). *Vicia cracca* L. (bird vetch) showed an accumulation capacity due to high shoot concentrations of Ba compared to the other species. Higher yield accompanied by a potential dilution effect can partly explain why *Trifolium repens* L. (white clover), *Pisum sativum* ssp. *arvénse* L. (gray pea) and *Hordeum vulgare* L. (barley) did not display the highest Ba concentrations, but showed the highest Ba uptake from soil. High plant uptake of calcium (Ca) also seemed to enhance Ba uptake, by legumes in particular. However, liming reduced shoot Ba concentrations, particularly of species with low affinity for Ca. The risk of Ba accumulation thus raises toxicity concerns when forage legumes are cultivated in soils containing elevated concentrations of Ba.

Key words: barium accumulation / bioconcentration / pot experiment / translocation

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1 Introduction

Barium (Ba) is an alkaline earth metal commonly present in plants, but without any known biological function (*Kabata-Pendias*, 2011). According to the World Health Organization (*WHO*, 1990), high soil concentrations of Ba are associated with limestone, feldspar, and shale deposits. Barium has been identified in over 80 minerals, but it occurs in significant quantities mainly in sparingly soluble forms such as barite ($BaSO_4$) or witherite ($BaCO_3$; *Boffito*, 1991; *DiBello* et al., 1991). Soil developed on bedrock containing these minerals may have high levels of Ba. For instance, near deposits of barite the concentration of Ba can be as high as 37 g kg^{-1} (*Adriano*, 1986). In terms of the source of Ba and its influence on plant Ba uptake, the element's characteristics are decisive for its availability. The solubility of Ba in soil tends to increase with decreasing pH (*Madejón*, 2013), under reducing conditions (*Magalhães* et al., 2014), and with microbial activity (*Coscione* and *Berton*, 2009). High cation exchange capacity (CEC) limits Ba mobility in the soil by adsorption (*Madejón*, 2013). In addition to availability in the growth medium, the plant species influences the plant content of an element (*Gjengedal* et al., 2015).

Most plants contain small amounts of Ba, but the concentration varies. *Coscione* and *Berton* (2009) found Ba concentrations in plants ranging from 4 to 50 mg kg^{-1}, whereas *Kabata-Pendias* (2011) reported mean Ba concentrations in different food and feed plants from 2 to 13 mg kg^{-1}. Some plants accumulate Ba, *e.g.*, legumes, grain stalks, forage plants, and Brazil nut trees (*Robinson* et al., 1950; *Choudhury* and *Cary*, 2001; *Prasad*, 2003, 2004; *Conçalves* et al., 2009; *Nogueira* et al., 2010). In a study on bush beans, *Wallace* and *Romney* (1971) observed reduced uptake of Ba with increasing levels of calcium (Ca) in the soil. This antagonistic effect of Ca on Ba uptake might be due to the formation of slightly soluble $BaCO_3$ and $BaSO_4$ (*Kabata-Pendias*, 2011). In a survey of native plants in a location with biotite-carbonatite bedrock at Stjernøy, Norway, plant uptake of Ba was closely related to uptake of Ca in the 29 species investigated (*Hillersøy*, 2010).

High concentrations of Ba (> 500 mg kg^{-1}) in trifoliate leaves of bush beans caused phytotoxicity symptoms (*Llugany* et al., 2000). A study on Tanzanian guinea grass reported symptoms on leaves indicating phytotoxicity at 225 mg kg^{-1} (*Monteiro* et al., 2011). *Suwa* et al. (2008) observed phytotoxic effects of Ba in soybean plants, expressed as inhibition of photosynthesis. Despite the low solubility of $BaSO_4$, uptake

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of Ba by test organisms from barite-contaminated soils induced phytotoxicity (*Lamb* et al., 2013). However, research on the mechanisms controlling Ba adsorption and uptake by plants from natural soils is scarce.

The aim of this study was to investigate the treatment effect of lime ($CaCO_3$) added to a Ba-containing sandy soil on uptake and interspecies distribution of Ba in legumes compared with other cultivated food and feed plants. Nine plant species, including grasses, herbs, vegetables, and legumes, were cultivated in a greenhouse experiment. In general, significant interspecies differences in plant Ba concentration were expected. Based on findings in the literature, the first hypothesis tested was: "Under similar growing conditions, legumes concentrate more Ba than grasses". Based on findings by *Hillersøy* (2010), the second hypothesis was: "Barium follows the Ca distribution pattern within the plant". The question of whether Ba uptake is directly correlated to Ca uptake or is the result of a confounding increase in pH led to the third hypothesis: "Under similar pH conditions, an increased supply of $CaCO_3$ reduces Ba uptake in plants grown in Ba-containing sandy soil".

2 Material and methods

2.1 Soil characteristics

An aeolian sand containing quartz and feldspar (1.3% clay/silt, 98% sand, d_{50} = 0.4 mm), originating from weathering of arkosic and granitic bedrock with a low total carbon content (0.015 wt%), was used for the study. Initially, 4.0 kg sand and 50 g peat were mixed in 3 dm^3 pots; *i.e.*, the growth medium contained about 1.3 wt% peat. Soil attributes before liming were: pH_{H2O}: 4.4; total phosphorus (P): 0.28 ± 0.064 g kg^{-1}; total S: 10 ± 5.4 mg kg^{-1}; CEC: 3.6 $cmol_{(c+)}$ kg^{-1}; base saturation (BS): 13%. Cation exchange capacity was calculated as the sum of protons, potassium (K), sodium (Na), Ca, and magnesium (Mg), while BS was calculated as the 'base' cation percentage fraction of CEC. Soil pH was adjusted by adding 100 mL 0.075 M sodium hydroxide (NaOH) to the control, and 0.50 g $CaCO_3$ (Emsure ® Reag. Ph. Eur. analytical reagent) to the lime treatment. After pH adjustment, pH_{H20} was approximately 6.3 (1 : 2.5 solid to solution ratio) in both the lime treatment and the control, a level of pH based on guidelines for the pH and BS relationship model developed by *Lathwell* and *Peech* (1964), referred to by *McFee* et al. (1977). Base saturation was expected to increase significantly. Reagents of analytical grade or better were used throughout and all water used was deionized (> 18 MΩ cm^{-1}).

2.2 Pot experiment

The species selected for the experiment were: barley (*Hordeum vulgare* L.), tall fescue (*Festuca arundinácea* Schreber L.), great mullein (*Verbascum thapsus* L.), carrot (*Daucus carota L.* ssp. *sativus*), radish (*Raphanus sativus* L.), spinach (*Spinacia oleracea* L.), gray pea (*Pisum sativum* ssp. *arvénse* L.), white clover (*Trifolium repens* L. Milkanova), and bird vetch (*Vicia cracca* L.) (*Lid* and *Lid*, 1994), each grown in four replicates. Great mullein was chosen as a potential accumulator of Ba (*Kowalska* et al., 2012). Bird vetch has shown great potential for Ba accumulation on soil developed on carbonatite bedrock (*Hillersøy*, 2010), and was therefore chosen as a Ba accumulator species. Gray pea was the only species not receiving any nitrogen (N) supplement, but was initially given 10 mL soil containing rhizobia. Tall fescue was harvested twice, after 9 and 13 weeks. Barley was harvested before development of grain (52 d of incubation) and

Table 1: Amounts of nitrogen (N), phosphorus (P), and potassium (K) added to each pot, based on recommendations for the individual species given by *Yara* (2015).

Species	**mL added**		
	N	**P**	**K**
	NH_4NO_3 12 g N L^{-1}	$Ca(H_2PO_4)_2 \times H_2O$ 3 g P L^{-1}	KCl 12 g K L^{-1}
Hordeum vulgare (barley)	25	17	17.5
Festuca arundinácea Schreb. (tall fescue)	15	10	7.5
Verbascum thapsus (great mullein)	15	10	7.5
Daucus carota ssp. *sativus* (carrot)	25	40	37.5
Raphanus sativus (radish)	20	30	25
Spinacia oleracea (spinach)	35	30	35
Trifolium repens (white clover)	15	20	12.5
Pisum sativum ssp. *arvense* (gray pea)[a]	0[a]	20	20
Vicia cracca (bird vetch)	15	10	7.5

[a] Gray pea received about 10 mL soil containing rhizobium bacteria.

in a separate lime-treated series ($n = 4$) after the grain had been fully developed (93 d).

Nutrient solutions of N, P, and K (Table 1) were initially added to each pot in concentrations relative to the requirement for each plant species (*Yara*, 2015). Pot bases were non-perforated. To avoid precipitation of $BaSO_4$, sulfate was replaced with chloride salts in some secondary macro and micronutrient solutions. To each pot, 10 mL of ZnCl (2.5 g L^{-1}) and 25 mL of each of $(NH_4)_6)Mo_4O_{24} \times 4\ H_2O$ (0.05 g L^{-1}), $Na_2B_4O_7 \times 10\ H_2O$ (0.25 g L^{-1}), $FeSO_4 \times 7\ H_2O$ (5.0 g L^{-1}), $MnSO_4$ (2.5 g L^{-1}), $CuSO_4 \times 5\ H_2O$ (2.5 g L^{-1}), and MgCl (12.5 g L^{-1}) were added. The soil water was kept near 60% of water-holding capacity by weighing each pot every second day and supplying deionized water throughout the experimental period. Plants were grown under controlled temperature and light conditions [temperature day (16 h): 19 ± 1°C; night (8 h): 16 ± 1°C]. In order to simulate daylight, 500 W lamps emitting yellow and white light in equal intensity, with an approximate photon flux of 200 μmol m^{-2} s^{-1} in daytime, were used.

2.3 Soil and plant analysis

The nitric acid-extractable Ba concentration in the peat was 3.8 ± 0.1 mg kg^{-1} ($n = 4$). The microwave technique (Milestone UltraClave 3) was used for digestion (approximately 0.250 g of accurately weighed samples; 25 min at maximum temperature 250°C; 65 wt% HNO_3, sub-boiled ultrapure) and ICP-OES (Perkin Elmer Optima 5300DV) for quantification. Total Ba concentration (X-ray fluorescence analysis; XRF) in the sand was 500 ± 6 mg kg^{-1}. Exchangeable base cations in soil, including Ba, were determined after extraction with 1 M ammonium acetate (pH 7.0; *Choudhury* and *Cary*, 2001; *Essington*, 2003). The Ba, Ca, and Mg concentrations were found to be 22, 70, and 15 mg kg^{-1}, respectively. The concentrations of K and Na were below the detection limit. The bioconcentration factor (BCF) was calculated according to:

$$BCF = \frac{Ba_{whole\ plant}\ (mg\ kg^{-1})}{Ba_{soil}\ (mg\ kg^{-1})}. \qquad (1)$$

Translocation of Ba from roots to shoots was calculated using the translocation index (TI):

$$TI = \frac{Ba_{shoots}\ (mg\ pot^{-1})}{Ba_{whole\ plant}\ (mg\ pot^{-1})}. \qquad (2)$$

Shoots were not divided into different organs with the exception of clover (stolons and leaves) and barley (93 d of incubation: culm, leaves, and grain). Shoots of all species and roots of barley, carrot, radish, spinach, and gray pea were dried at 45°C. Before drying, roots were rinsed with de-ionized water. Approximately 0.250 g of accurately weighed, milled and sieved (2 mm) dry sample was then digested at 250°C with nitric acid (65 wt% HNO_3, sub-boiled ultrapure) using the microwave technique. The plant content of 64 elements was determined using ICP-MS (Agilent 8800 Triple Quadrupole) and ICP-OES (Perkin Elmer Optima 5300DV), but only the results for Ba and Ca are presented in this study.

Accuracy was checked by simultaneous analysis of standard reference materials: NCS DC 73348 Bush twigs and leaves, International Atomic Energy Agency (IAEA) V-10 Hay, NIST 2709a San Joaquin Soil, and NIST 2711a Montana II Soil. Allowing for experimental error, our data were within the recommended or standard values. Intermediate precision (within-laboratory reproducibility; $n = 4$) reflected variation associated with, *e.g.*, nonhomogeneous growth medium. The relative standard deviation (RSD) in dry weight ranged from 4 to 22% except for bird vetch and great mullein, for which RSD ranged from 33 to 44%. The RSD obtained for Ba concentration in shoots and roots ranged from 2 to 25% and 9 to 28%, respectively.

2.4 Statistics

Given equilibrium conditions, the concentration of an element in soil and its transfer to plants may be assumed to show a linear relationship (*Chojnacka* et al., 2005; *Abreu* et al., 2012). Two-factor regression including interaction was used here to investigate interspecies differences and effect of lime treatment. In addition, ANOVA, Student's t-test, and Tukey's family-wise test (95% CL) were performed using the software $R_{x64\ 301}$ and $R_{commander}$ (*Faraway*, 2002).

3 Results

3.1 Uptake of Ba by plants

All the test plants had measurable amounts of Ba in their tissues. The concentrations of Ba differed widely among species and showed a significant ($P < 0.1\%$) interaction with liming (Fig. 1). Average shoot Ba concentration of the nine species ranged from about 100 to 600 mg kg^{-1} (Table 2). In control soil, bird vetch and white clover accumulated Ba to a higher concentration than the other species, while in lime-treated soil only bird vetch showed a similar response [Tukey's test, 95% confidence level (CL), $P < 0.1\%$; Fig. 1a]. Average root Ba concentration ranged from about 100 (carrot) to 700 mg kg^{-1} (gray pea). Gray pea had significantly higher root Ba concentrations in both control soil and lime-treated soil than carrot, radish, and spinach (Tukey's test, 95% CL, $P < 0.1\%$) (Fig. 1c).

Average shoot dry weight (DW) ranged from 2 to 27 g, while DW of roots ranged from 0.8 to 12 g (Table 2). The highest shoot DW was observed for barley and the highest root DW for carrot. An increase in DW was negatively correlated with Ba concentration in shoots in the control ($r^2 = 0.20$, $n = 38$, $P = 0.5\%$; Fig. 2a) and the lime-treated soil ($r^2 = 0.40$, $n = 39$, $P < 0.1\%$; Fig. 2c), and in roots in the control ($r^2 = 0.45$, $n = 15$, $P = 0.6\%$; Fig. 2b) and lime-treated soil ($r^2 = 0.56$, $n = 13$, $P = 0.2\%$; Fig. 2d). The large interspecies variation in DW was taken into account in the two-factor regression model using total Ba uptake adjusted for DW (μg Ba pot^{-1} DW) as the response variable. In the control, barley, white clover, and gray pea had significantly higher Ba contents in shoots than the other species, while in the lime treatment higher Ba contents were observed in barley and gray pea shoots (Tukey's test, 95% CL, $P < 0.1\%$; Fig. 1c). Content of Ba in roots (both

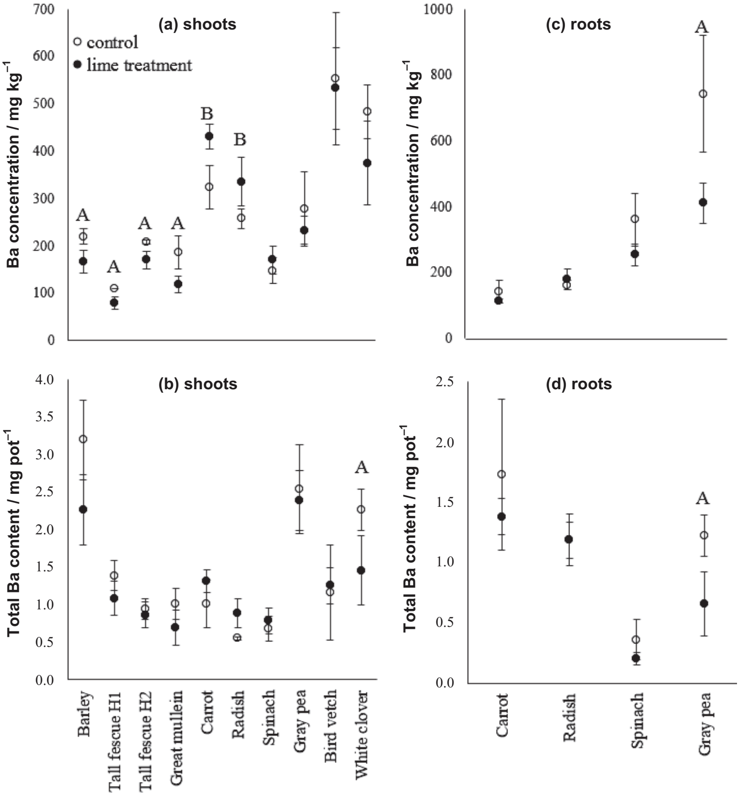

Figure 1: Mean (a) concentration of Ba (mg kg^{-1}), (b) total Ba content (mg pot^{-1}) in shoots of nine species, (c) concentration of Ba (mg kg^{-1}), and (d) total Ba content (mg pot^{-1}) of roots of four species in control and lime treatments. Bars represent standard deviation. Letters represent: A– significant reduction in Ba concentration by liming ($P < 5\%$), and B–significant increase in Ba concentration by liming ($P < 5\%$).

control and treatment) of gray pea was not significantly different from that in roots of carrot and radish (Fig. 1d). The bioconcentration factor (BCF) of Ba in the different plant species ranged from 5 to 33 in roots, and from 5 to 25 in shoots. Translocation from roots to shoots based on the total content of Ba per pot ranged from about 30 to 80% (Table 3).

3.2 Within-plant distribution pattern of Ba and Ca

Initially, pH in the control and lime treatment was adjusted with NaOH and $CaCO_3$, respectively, to about 6.3. By the time of harvest, pH ranged from about 5 to 6 (data not shown) and no confounding pH effect on Ba concentration was found. Shoot concentrations of Ba and Ca in all species were positively correlated for the control ($r^2 = 0.57$, $n = 40$, $P < 0.1\%$) and lime treatment ($r^2 = 0.64$, $n = 40$, $P < 0.1\%$; Fig. 3a). In roots of four species, Ba and Ca correlated well in the control ($r^2 = 0.89$, $n = 16$, $P < 0.01\%$) and the lime treatment ($r^2 = 0.95$, $n = 15$, $P < 0.1\%$) (Fig. 3b). Barley, tall fescue, and great mullein had markedly lower Ca concentrations in their shoot tissue than the other species (Table 2).

3.3 Effect of liming on uptake of Ba by plants

There was increased plant uptake of Ca following addition of $CaCO_3$ to soil (Table 2). The mean Ba : Ca ratio in shoots (pair-wise t-test, 95% CL, $P < 0.1\%$) and roots (pair-wise t-test, 95% CL, $P < 0.1\%$) was significantly lower in the lime treatment than in the control. Considering shoot tissue (Fig. 1a) of spinach, gray pea, and bird vetch, no effect of liming on Ba concentration was found (pair-wise test, 95% CL; Pv > 5%). However, in shoots of barley, tall fescue, and great mullein, a decreased concentration of Ba was observed ($P < 5\%$), whereas an increase in Ba concentration was observed in carrot ($P < 5\%$) and an increasing tendency in radish ($P = 6\%$). Liming decreased Ba concentration in stolons of white clover ($P < 0.1\%$), but in trifoliate leaves no effect was detected ($P = 15\%$). In roots, liming decreased the Ba concentration in gray pea ($P < 5\%$), a decreasing tendency was observed in spinach ($P = 8\%$), and in carrot and radish no effect was observed (Fig. 1c). An increase in shoot Ba concentration, bioconcentration factor and translocation of Ba from roots to shoots were observed (Table 3). With regard to total Ba content (mg pot^{-1}), shoots of white clover showed a significant decrease after addition of lime ($P = 4\%$) but no significant effect of liming was observed in the other species, neither shoots nor roots (Fig. 1b, d).

Table 2: Plant dry weight (DW), barium (Ba) concentration, total content of Ba in plants, and relative distribution [$Ba_{plant\ part(mg/pot)}/Ba_{whole\ plant(mg/pot)}$] in different organs of nine plant species; n = 4 except for roots of barley, for which n = 1.[a]

Plant species	Seed per pot	Growth durat. / d	Plant part	DW / g		Ba concentration / mg kg^{-1}		Ca concentration / g kg^{-1}		Total Ba content / mg pot^{-1}		Relative Ba distribution / %	
				Lime	Control	Lime	Control	Lime	Control	Lime	Control	Lime	Control
Hordeum vulgare (barley)	8	52	Root	n.d	6.5	n.d	130	n.d	2.5	n.d	0.85	n.d	21
			Shoot	14 ± 1.8	15 ± 1.6	170 ± 24	220 ± 14	5. ± 1.0	2.9 ± 0.3	2.3 ± 0.47	3.1 ± 0.47	n.d	79
Hordeum vulgare	8	93	Grain	16 ± 1.0	n.d	55 ± 3.9	n.d	0.7 ± 0.04	n.d	0.90 ± 0.11	n.d	26	n.d
			Stem	4.1 ± 0.19	n.d	91 ± 7.8	n.d	1 ± 0.1	n.d	0.37 ± 0.022	n.d	11	n.d
			Leaf	7.0 ± 0.26	n.d	310 ± 8.2	n.d	8 ± 0.8	n.d	2.16 ± 0.025	n.d	63	n.d
Festuca arundinácea Schreb. (tall fescue)	12	66	Shoot$_{H1}$	14 ± 1.0	13 ± 1.8	80 ± 14	110 ± 0	3.8 ± 0.5	2.2 ± 0.2	1.1 ± 0.23	1.40 ± 0.20	n.d	n.d
		104	Shoot$_{H2}$	5.1 ± 0.51	4.5 ± 0.62	170 ± 18	208 ± 5.0	3.5 ± 0.3	2.2 ± 0.1	0.87 ± 0.17	0.94 ± 0.14	n.d	n.d
Verbascum thapsus (great mullein)	3	130	Leaf	6 ± 2.7	6 ± 2.1	120 ± 17	200 ± 35	8.6 ± 0.7	7.5 ± 0.4	0.7 ± 0.22	2.0 ± 1.2	n.d	n.d
Daucus carota ssp.sativus (carrot)	4	80	Root	12 ± 1.5	12 ± 2.9	110 ± 6	140 ± 35	1.5 ± 0.07	1.2 ± 0.02	1.4 ± 0.15	1.7 ± 0.62	52	64
			Shoot	3.1 ± 0.24	3.1 ± 0.60	430 ± 27	320 ± 46	19.8 ± 1.2	12.1 ± 1.6	1.3 ± 0.16	1.0 ± 0.32	48	36
Raphanus sativus (radish)	4	37	Root	6.7 ± 0.11	7.4 ± 0.57	180 ± 31	160 ± 14	2.4 ± 0.21	1.8 ± 0.09	1.2 ± 0.22	1.2 ± 0.15	57	68
			Shoot	2.7 ± 0.34	2.2 ± 0.15	340 ± 52	260 ± 21	18.7 ± 1.5	11.5 ± 1.3	0.9 ± 0.19	0.55 ± 0.024	43	32
Spinacia oleracea (spinach)	4	37	Root	0.8 ± 0.12	1.0 ± 0.27	250 ± 34	360 ± 80	3.4 ± 0.33	2.8 ± 0.21	0.21 ± 0.052	0.4 ± 0.17	21	35
			Shoot	4.6 ± 0.63	5 ± 1.0	170 ± 29	150 ± 28	18.9 ± 0.6	9.3 ± 0.8	0.8 ± 0.18	0.7 ± 0.17	79	65
Pisum sativum arvense (gray pea)	4	52	Root	1.6 ± 0.44	1.7 ± 0.26	400 ± 120	700 ± 180	6.8 ± 0.60	5.9 ± 0.55	0.7 ± 0.26 2.4 ± 0.40	1.2 ± 0.17	45	33
			Shoot	10.0 ± 0.92	9.3 ± 0.50	260 ± 60	280 ± 80	14.9 ± 0.7	10.0 ± 2.2		2.5 ± 0.60	55	67
Trifolium repens (white clover)	4	59	Stolon	0.77 ± 0.060	0.9 ± 0.19	500 ± 100	810 ± 96	10 ± 0.8624 ± 2.7	6.6 ± 0.97	0.40 ± 0.091	0.73 ± 0.066	27	31
			Leaf	3.1 ± 0.40	3.8 ± 0.16	340 ± 90	410 ± 65		14 ± 1.6	1.1 ± 0.38	1.6 ± 0.26	73	69
Vicia cracca (bird vetch)	4	80	Shoot	2.4 ± 0.10	2.0 ± 0.68	530 ± 87	600 ± 140	22.6 ± 2.4	15.7 ± 3.4	1.3 ± 0.24	1.2 ± 0.64	n.d	n.d

[a] H1 = first harvest, H2 = second harvest from the same pots; n.d = no data.

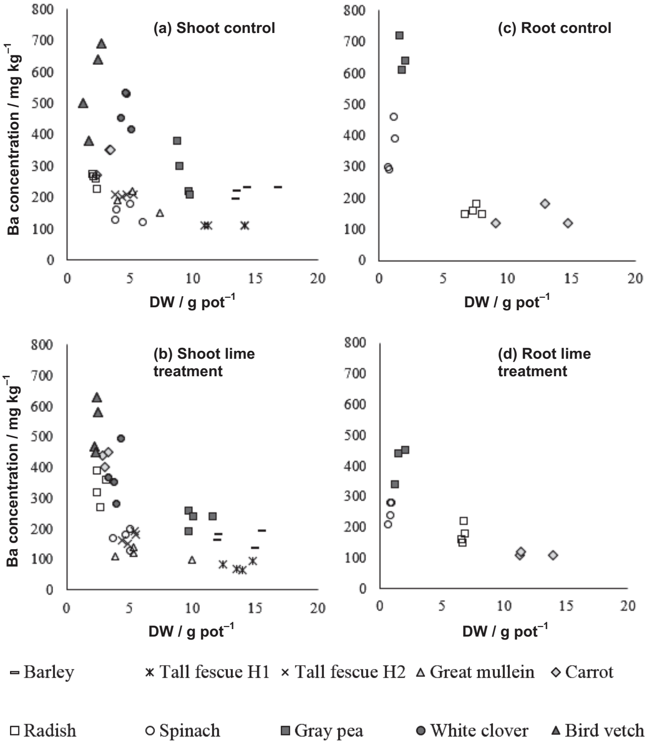

Figure 2: Barium (Ba) concentration related to dry weight (DW) of shoots in the (a) control, and (b) lime treatment, and of roots in the (c) control and (d) lime treatment. H1: first harvest, and H2: second harvest from the same pots.

4 Discussion

4.1 Uptake and distribution of Ba in plants

Tissue Ba concentrations of white clover and bird vetch (Table 2) exceeded the lowest observed effective concentration for toxicity (LOEC) reported for bush bean (*Llugany* et al., 2000) and Tanzanian guinea grass (*Monteiro* et al., 2011). The considerable differences in Ba concentrations between bird vetch and tall fescue may have been an effect of dilution, as the total Ba uptake did not differ between these two species. By definition, accumulation is the ability of a plant to accumulate an element to higher tissue concentrations than the concentration in the growth medium. Thus, bird vetch can be defined as a Ba accumulator as also observed by *Hillersøy* (2010). The Ba concentration of barley grain and white clover was about 10 and 35 times higher than the concentration of the respective species reported by *Kabata-Pendias* (2011). For the plant species included in the present work, no toxic effect caused by Ba has been reported in literature, except for barley. Average shoot Ba concentration in barley (harvested after 93 d) was equivalent to about 0.01% of plant DW, which was about 100-fold lower than the concentration reported to induce considerable yield decreases in barley (*Chaudhry* et al., 1977).

Table 3: Bioconcentration factor (BCF), expressed as the ratio of barium (Ba) concentration in roots and shoots compared with exchangeable Ba in soil, and translocation index (TI), expressed as the ratio of Ba content in shoots compared with Ba content in the whole plant, calculated for selected plant species; $n = 4$ except for roots of barley, for which $n = 1$.[a]

Plant species	BCF Roots (Ba)		BCF Shoots (Ba)		TI% (Ba)		TI% (Ca)	
	Control	Lime	Control	Lime	Control	Lime	Control	Lime
Barley	6	n.d	10	8*	81	n.d	72	n.d
Tall fescue	n.d	n.d	6	5*	n.d	n.d	n.d	n.d
Great mullein	n.d	n.d	11	5*	n.d	n.d	n.d	n.d
Carrot	6	5	15	20*	37 ± 3.1	49* ± 0.7	71 ± 1.7	77* ± 0.8
Radish	7	8	12	15*	32 ± 3.1	43* ± 0.8	65 ± 2.9	75* ± 2.1
Spinach	16	12	7	8	67 ± 6.4	79* ± 3.0	94 ± 1.3	97* ± 0.5
Gray pea	33	19*	13	11	67 ± 4.3	80* ± 7.6	90 ± 2.7	94 ± 2.2
White clover	n.d	n.d	22	17	n.d	n.d	n.d	n.d
Bird vetch	n.d	n.d	25	24	n.d	n.d	n.d	n.d

[a] $BCF = Ba_{\text{whole plant (mg /kg)}}/Ba_{\text{soil (mg/kg);}}$ $TI = Ba_{\text{shoots (mg/pot)}}/Ba_{\text{whole plant (mg/pot)}}$; Asterisks represent significant differences compared with controls ($P < 5\%$).

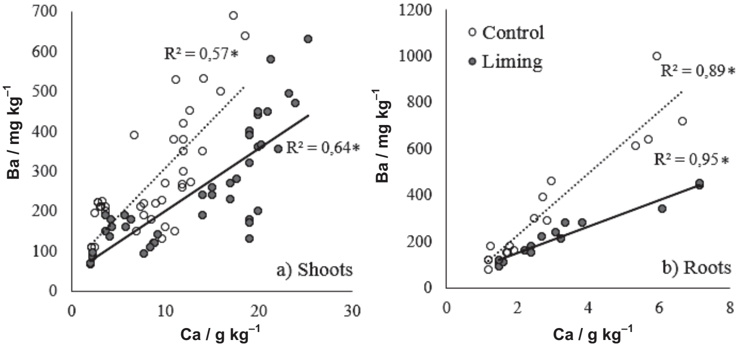

Figure 3: Relationship between barium (Ba) and calcium (Ca) (a) in shoots of nine species in the control ($F_{1,38}$ = 69, $P < 0.1\%$) and lime treatment ($F_{1,38}$ = 50, $P < 0.1$); and (b) in roots of four species in the control ($F_{1,14}$ = 116, $P < 0.1\%$) and lime treatment ($F_{1,13}$ = 252, $P < 0.1\%$). Effect of individual species not shown. Asterisks represent significance ($P < 0.1\%$).

Even though the legumes in this experiment had notably higher concentrations of Ba than the grasses, the differences in Ba acquisition potential from soil are probably negligible, as the total Ba content in barley did not differ from that in gray pea and white clover, and the total Ba content in tall fescue did not differ from that in bird vetch. Great mullein was not considered a Ba accumulator in our experiment. *Kowalska* et al. (2012) found Ba concentrations of leaf rosette and stem of *Verbascum densiflora* of about 340 and 35 mg kg^{-1}, respectively, but under growth conditions and potential contributing factors (*e.g.*, field research design, climate conditions) that differed greatly from those in our experiment. The *Verbascum thapsus*, referred to as great mullein in our study, was the only biennial plant included, with leaves harvested at the leaf rosette stage. Analyses of Ba content in the stem after second-year flowering would be of interest due to potential redistribution of Ba.

4.2 Factors controlling Ba availability to plants

Variations in plant Ba contents in this experiment may reflect the importance of considering factors controlling Ba availability such as soil, growth conditions, and Ba source. Most previous experiments on plant uptake of Ba have been in hydroponics or soils spiked with soluble Ba salts (*e.g.*, *Llugany* et al., 2000; *Suwa* et al., 2008; *Melo* et al., 2011). Due to similar ionic radius, Ba follows the K-fate in geochemical processes (*Kabata-Pendias*, 2011), and thus, probably substitutes for K in the silica lattice of the sparingly soluble K-feldspars (*Heier*, 1962). The sand used here was assumed to give more realistic prediction of Ba uptake, as the Ba taken up by plants mainly originates from exchangeable sites on the surface of feldspar particles, which represented about 30% of the sand. The relatively high ability of the plants to absorb Ba was probably related to the low CEC and low nutrient retention ability of the sandy soil (*Melo* et al., 2011).

The soil contained only minor amounts of sulfur (S) and organic matter (OM) and thus precipitation of $BaSO_4$ and adsorption of Ba to OM was limited. In soils containing high levels of sulfate, OM, or cation exchange sites, like clay, Ba is likely to be less available to plants due to adsorption (*Madejón*, 2013). High manganese (Mn) concentrations (results not shown), up to 3 and 5 g kg^{-1} of shoots of bird vetch and carrot, respectively, indicated reducing conditions, which might be explained by the non-perforated pots and the compactness of the soil. Reducing conditions can make Ba more available in the soil (*Madejón*, 2013). According to findings by *Hillersøy* (2010), bird vetch shows great potential for Ba accumulation also when grown in a natural habitat, and thus reducing conditions is not a likely explanation for the high Ba concentrations. *Gupta* et al. (1970) reported high resistance to Mn toxicity (> 7 g kg^{-1}) in carrot (*El-Jaoual* and *Cox*, 1998), and thus a minor reduction in plant yield was expected in this experiment.

The bioconcentration factor (BCF) for Ba was calculated mainly to compare species cultivated under similar conditions. The calculated value of exchangeable Ba in soil is most likely an overestimation of the actual bioavailable Ba content, since not all exchangeable Ba in the soil is readily available to plant roots. Thus, the BCF (Table 3) is probably an underestimation of Ba absorption. However, underestimation of BCF is a systematic error not influencing relative comparisons of BCF. Any contribution to uncertainty in translocation index (TI; Table 3) due to incorporation of soil particles into roots and subsequent overestimation of the root Ba content was unlikely, as demonstrated by the satisfactory intermediate precision obtained. The high uptake and bioconcentration of Ba obtained in roots of gray pea (Tables 2 and 3) was explained by high CEC in roots and a potential influence of rhizobium activity. Gray pea relies on biological N_2 fixation, as demonstrated by large amounts of active nodules on the roots. The lower Ba concentrations in roots of radish and carrot (Table 2), in contrast to spinach and gray pea, were probably related to a dilution effect, due to differing root structure. This might be confirmed by the total Ba uptake expressed in terms of DW (mg Ba pot^{-1}), which showed an opposite trend to plant Ba concentration (mg kg^{-1}; Fig. 1).

4.3 Effect of liming on Ba uptake in plants

The positive correlation of Ba concentration with Ca (Fig. 3) provides strong evidence that Ba closely follows Ca uptake and distribution in plant tissues, supporting findings by *Hillersøy* (2010). In general, uptake of Ba from the soil seems to be slightly suppressed by liming, as demonstrated by the lower Ba : Ca ratio in lime-treated species. The negative response to liming of Ba concentration of shoots of barley, tall fescue, and great mullein is in agreement with findings by *Wallace* and *Romney* (1971) and *Kabata-Pendias* (2011). However, the strategy for uptake of Ca and Ba varied between species and plant parts, as shown previously by *Wallace* and *Romney* (1971).

The N, P, and K fertilization requirements vary among the species selected for this experiment. The soluble P fertilizer included some Ca and probably facilitated Ca uptake and potentially higher Ba uptake in carrot in particular, as this species requires four times more P than, *e.g.*, tall fescue. The non-response to liming of shoot Ba concentrations of gray pea and spinach was explained by lower root uptake and simultaneously elevated translocation of Ba and Ca from roots to shoots. Increased translocation of Ba and Ca in carrot and radish caused by liming may also explain the elevated Ba concentration in the shoots. Considering tuber vegetables for food, the translocation of Ba to non-edible plant parts by liming is promising. The general increase in Ba translocation from roots to shoots combined with the ambiguous Ba response in different plant species to liming reflects the complex relationship between the antagonistic effect of Ca on Ba transfer from soil to roots and the distribution relationship between these two elements within plants. The low Ca uptake in barley, tall fescue, and great mullein partly agrees with findings by *Loneragan* and *Snowball* (1969), who demonstrated higher affinity for Ca in legumes and herbs than in grasses and cereals. As Ba seems to follow Ca uptake and distribution, the high Ca affinity observed for carrot, radish, spinach, gray pea, and bird vetch may give an indication as to why Ba concentrations in shoots were not significantly depressed by liming. This study provides evidence to suggest that liming reduces Ba uptake in species with low affinity for Ca.

5 Conclusions

All plant species studied were able to take up Ba from the sparingly soluble K-feldspar in the soil, with tissue concentrations ranging from about 100 (tall fescue) to 600 mg kg^{-1} (bird vetch) in shoots and from about 100 (carrot) to 700 mg kg^{-1} (gray pea) in roots. All the legumes had notably higher concentrations of Ba in their shoot tissues than the grasses, with the highest Ba accumulation potential in bird vetch. However, total Ba uptake from soil did not differ among gray pea, white clover, and barley, or between tall fescue and bird vetch. Plant tissue concentrations of Ba and Ca correlated well, supporting the hypothesis that Ba follows Ca uptake in plants. Liming decreased shoot Ba concentrations mainly in species with low affinity for Ca, *i.e*., tall fescue, barley, and great mullein. Thus, the hypothesis that liming in general reduces Ba uptake by plants was not confirmed. A risk of Ba accumulation and potential toxicity in forage legumes grown in soils naturally rich in Ba demands further research on other factors controlling Ba mobility in soil, *e.g.*,, soil organic matter, pH, and microbial activity.

References

Abreu, C. A., *Cantoni, M.*, *Coscione, A. R.*, *Paz-Ferreiro, J.* (2012): Organic matter and barium absorption by plant species grown in an area polluted with scrap metal Residue. *J. App. Environ. Soil Sci.* 2012. DOI: 10.1155/2012/476821

Adriano, D. C. (1986): Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, NY, USA, pp. 472–473.

Boffito, C. (1991): Barium, in Seidel, A. (ed.): Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition. John Wiley and Sons, New York, NY, USA, pp. 902–908.

Chaudhry, F. M., *Wallace, A.*, *Mueller, R. T.* (1977): Barium toxicity in plants. *Commun. Soil Sci. Plan.* 8, 795–797.

Chojnacka, K., *Chonjacki, A.*, *Górecka, H.*, *Górecki, H.* (2005): Bioavailability of heavy metals from polluted soils to plants. *Sci. Total Environ.* 337, 175–182.

Choudhury, H., *Cary, R.* (2001): Barium and barium compounds. World Health Organization, Geneva, Switzerland. Available at: http://www.inchem.org/documents/cicads/cicads/cicad33.htm.

Conçalves, A. M., *Fernandes, K. G.*, *Ramos, L. A.*, *Cavalheiro, É. T. G.*, *Nóbrega, J. A.* (2009): Determination and fractionation of barium in Brazil nuts. *J. Braz. Chem. Soc.* 20, 760–768.

Coscione, A. R., *Berton, R. S.* (2009): Barium extraction potential by mustard, sunflower and castor bean. *Sci. Agric.* 66, 59–63.

DiBello, P. M., *Manganaro, J. L.*, *Aguinaldo, E. R.* (1991): Barium Compounds, in Seidel, A. (ed.): Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition. John Wiley and Sons, New York, NY, USA, pp. 909–930.

El-Jaoual, T., *Cox, D. A.* (1998): Manganese toxicity in plants. *J. Plant Nutr.* 21, 353–385.

Essington, M. E. (2003): Soil and Water Chemistry—An Integrative Approach. CRC Press, Boca Raton, FL, USA.

Faraway, J. J. (2002): Practical regression and anova using R. Available at: http://www.mathstat.ualberta.ca/~wiens/stat568/misc%20resources/Faraway-PRA.pdf.

Gjengedal, E., *Martinsen, T.*, *Steinnes, E.* (2015): Background levels of some major, trace, and rare earth elements in indigenous plant species growing in Norway and the influence of soil acidification, soil parent material, and seasonal variation on these levels. *Environ. Monitor. Assess.* 187, 386–414.

Gupta, U. C., *Chipman, E. W.*, *MacKay, D. C.* (1970): Influence of manganese and pH on chemical composition, bronzing of leaves, and yield of carrots grown on acid sphagnum peat soil. *Soil Sci. Soc. Am. J.* 34, 762–764.

Heier (1962): Trace elements in feldspars– a review. *Norsk Geol. Tidsskr.* 42, 415–454.

Hillersøy, M. (2010): Plant uptake of barium and strontium in areas with biotite-carbonatite bedrock at Stjernøy, Alta, Norway. Master thesis, Norwegian University of Life Sciences, Norway.

Kabata-Pendias, A. (2011): Trace Elements in Soils and Plants, 4th Ed. CRC Press, Boca Raton, FL, USA, pp. 142–144.

Kowalska, J., *Stryjewska, E.*, *Bystrzejewska-Piotrowska, G.*, *Lewandowski, K.*, *Tobiasz, M.*, *Paldyna, J.*, *Golimowski, J.* (2012): Studies of plants useful in the re-cultivation of heavy metals-contaminated wasteland -a new hyperaccumulator of barium? *Pol. J. Environ. Stud.* 21, 401–405.

Lamb, D. T., *Matanitobua, V. P.*, *Palanisami, T.*, *Megharaj, M.*, *Naidu, R.* (2013): Bioavailability of barium to plants and invertebrates in soils contaminated by barite. *Environ. Sci. Technol.* 47, 4670–4676.

Lathwell, D. J., *Peech, M.* (1964): Interpretation of Chemical Soil Tests. Cornell Univ. Agr. Exp. Sta. Bull. No. 995. Cornell University, Ithaca, NY, USA.

Llugany, M., *Poschenrieder, C.*, *Barceló, J.* (2000): Assessment of barium toxicity in bush beans. *Arch. Environ. Contam. Tox.* 39, 440–444.

Lid, J., *Lid, D. T.* (1994): Norsk Flora, 6th Ed. Det Norske Samlaget, Oslo, Norway.

Loneragan, J. F., *Snowball, K.* (1969): Calcium requirements of plants. *Aust. J. Agric. Res.* 20, 465–477.

Madejón, P. (2013): Barium, in Alloway, B. J. (ed.): Heavy Metals in Soils—Trace Metals and Metalloids in Soils and their Bioavailability, 3rd Ed. Springer, Heidelberg, Germany, pp. 507–513.

Magalhães, M. O. L., *Sobrinho, N. M. B. A.*, *Zonta, E.*, *Becerra, A. T.*, *Lastra-Bravo, X. B.*, *Coutinho, I. B.* (2014): Reducing conditions on barium absorption in rice plants cultured in $BaSO_4$-enriched soil. *Acta Scient. Agron.* 36, 119–127.

McFee, W. W., *Kelly, J. M.*, *Beck, R. H.* (1977): Acid precipitation effects on soil pH and base saturation of exchange sites. *J. Water Air Soil Poll.* 7, 401–408.

Melo, L. C. A., *Alleoni, L. R. F.*, *Carvalho, G.*, *Azevedo, R. A.* (2011): Cadmium- and barium-toxicity effects on growth and antioxidant capacity of soybean (*Glycine max* L.) plants, grown in two soil types with different physicochemical properties. *J. Plant Nutr. Soil Sci.* 174, 847–859.

Monteiro, F. A., *Nogueirol, R. C.*, *Melo, L. C. A.*, *Artur, A. G.*, *da Rocha, F.* (2011): Effect of barium on growth and macronutrient nutrition in Tanzania guineagrass grown in nutrient solution. *Commun. Soil Sci. Plan.* 42, 1510–1520.

Nogueira, T. A. R., *deMelo, W. J.*, *Fonseca, I. M.*, *Marques, M. O.*, *He, Z.* (2010): Barium uptake by maize plants as affected by sewage sludge in a long-term field study. *J. Hazard. Mater.* 181, 1148–1156.

Prasad, M. N. V. (2003): Phytoremediation of meta-polluted ecosystems: hype for commercialization. *Russ. J. Plant Physiol.* 50, 686–699.

Prasad, M. N. V. (2004): Heavy Metal Stress in Plants—From biomolecules to Ecosystems, 2nd Ed. Springer-Verlag, Berlin, Germany.

Robinson, W. O., *Whetstone, R. R.*, *Ergington, G.* (1950): The occurrence of barium in soils and plants. *U.S. Dept. Agric. Tech. Bull.* 1013, 1–36.

Suwa, R., *Jayachandran, K.*, *Nguyen, N. T.*, *Boulenouar, A.*, *Fujita, K.*, *Saneoka, H.* (2008): Barium toxicity effects in soybean plants. *Arch. Environ. Contam. Toxicol.* 55, 397–403.

Wallace, A., *Romney, E. M.* (1971): Some interactions of Ca, Sr and Ba in plants. *Agron. J.* 63, 245–248.

WHO–World Health Organization (1990): Environmental health criteria 107: Barium. International Programme on Chemical Safety, Geneva, Switzerland. Available at: http://www.inchem.org/documents/ehc/ehc/ehc107.htm.

Yara (2015): Gjødselhåndbok 2014/15. Yara Norway AS. Oslo, Norway. Available at: https://yaraurl.com/hnd0.

Paper III

The use of carbonatite rock powder as a liming agent

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Use of carbonatite rock as fertilizer and liming agent, and uptake of Ba, Sr, Ca, Mg and K to *Festuca arundinácea* and *Trifolium repens* on increasing the supply of peat

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Abstract

Carbonatite rock powder originating from the Lillebukt Alkaline Complex at Stjernøy in northern Norway can potentially be used as a slow-releasing lime and potassium (K) fertilizer, due to a high content of the easily weathered minerals calcite (42 wt%) and biotite (30 wt%). However, the enrichment of barium (3 g Ba kg^{-1}) and strontium (4 g Sr kg^{-1}) may cause an undesired uptake to plants when carbonatite is applied to agroecosystems. A pot experiment was designed to investigate the liming and K-fertilization effect of carbonatite and the potential mobilization of Ba and Sr compared to a dolomite lime commonly used in Norwegian agriculture. These liming agents were mixed with a sandy soil applied to different amounts of peat, and the uptake of Ba, Sr, calcium (Ca), magnesium (Mg) and K uptake in *Festuca arundinácea* Schreb. (tall fescue) and *Trifolium repens* L. (white clover) were evaluated. The liming agents were generally incapable of buffering the acidifying effect from increased applications of peat, while the plant dry mass was unaffected. Compared to pots given dolomite and soluble K, the availability of K from carbonatite to plants was equally high or higher, and no difference in the K/(Ca+Mg) ratio in plants was observed. Carbonatite was a significant source to plant Ba and Sr, and the uptake seemed to follow the Ca uptake. Addition of peat amplified the uptake of Ba, Sr, Ca, Mg and K to plants, probably an effect of organic acid-induced weathering of carbonatite. White clover took up Ba, Sr and Ca more effectively than tall fescue, but the Ba and Sr concentrations in plants were relatively moderate compared to concentrations reported from field investigations. The pot experiment should be accompanied by field trials to investigate the impact of climatic conditions, leaching and runoff on the nutrient balance when carbonatite is used as a soil conditioner.

1 Introduction

Due to its multifarious content of essential nutrients (*Heim*, 2001), carbonatite rock from the Lillebukt Alkaline Complex at Stjernøy in northern Norway (70° 17.75’ N, 22° 34.5’ E) possesses fertilizing and liming characteristics. The main minerals are calcite (~40 wt%), biotite (~30 wt%), apatite (~7 wt%) and nepheline (*Gautneb*, 2009; *Heim* et al., 2012). The Spanish River Carbonatite in Canada has been mined for several years for its use as a natural mineral fertilizer and soil conditioner in bulk agricultural markets (http://www.borealagrominerals.com/). The carbonatite at Stjernøy possesses similar characteristics. Although the calcite content is somewhat lower, Stjernøy carbonatite provides a liming effect when applied to acid soils (*Bakken* et al., 1997). Compared to the Spanish River Carbonatite, the biotite fraction in the Stjernøy carbonatite is higher, thereby providing a nutritional supply of both K and Mg when applied to soil. Potassium deriving from the biotite and nepheline fraction in carbonatite has been shown to be utilized by plants in significant amounts (*Bakken* et al., 1997). But it has also been demonstrated in field trials that the kinetic release of K during carbonatite weathering can be too slow to fully replenish the available pool of K in soil removed by plants (*Bakken* et al., 2000). The minerals in carbonatite rock are low in toxic and radiogenic metals, e.g. cadmium (Cd) and lead (Pb), though concurrently high concentrations of barium (Ba; 3.2 g kg^{-1}) and strontium (Sr; 4.2 g kg^{-1}) have been reported (*Heim* et al., 2012). Barium in soils is usually derived from K-bearing minerals such as K-feldspars and biotite, and due to their similar ionic radii, Ba follows the geochemistry of K (*Madejón*, 2013; *Kabata-Pendias*, 2011). Since Ba is highly concentrated in the biotite fraction of the carbonatite rock in particular (5.5 g kg^{-1} in average), natural weathering adds Ba to the soil. The Sr is primarily associated with the calcite fraction of the carbonatite, in which up to 90% of the Sr is bound (*Strand*, 1981). When carbonatite is applied as a soil conditioner, the weathering may lead to an undesired Ba and Sr uptake by plants.

We designed a pot experiment growing white clover and tall fescue as test crops to investigate the liming effect of carbonatite compared to dolomite, in addition to the uptake of Ca, K, Mg, Ba and Sr to plants grown on sandy soil mixed with peat. We hypothesize that: i) Carbonatite is as equally strong of a liming agent as dolomite to help buffer the pH when the organic acid content of the growth media increases; ii) There will be no difference in yield when applying equally effective liming amounts of dolomite or carbonatite to soil. Justified by the biogeochemical similarities of Ba, Sr and Ca (*Marschner*, 2012), we believe that: iii) Plants with a high affinity for Ca, such as legumes, will have a correspondingly high affinity for Ba and Sr, and the application of carbonatite will increase the uptake of these elements; and iv) Carbonatite application to soil will increase the geochemically labile K concentrations and create an imbalance between K-Mg-Ca in plants, compared to when only dolomite is applied.

2 Material and Methods

2.1 Soil characteristics

An aeolian sand containing quartz and feldspar (1.3% clay/silt, 98% sand, d50 = 0.4mm) weathered from arkosic and granitic bedrock with a low carbon content (0.015 weight, wt%), was used. Initially, 2.1 kg (dry weight, dw.) of sand was mixed with 50, 200 and 500 g (dw.) of unfertilized peat (equal to approximately 2, 10 and 20 wt% peat) in non-perforated 3 dm^{-3} pots. Inert polystyrene balls were added to pots filled with 2 and 10 wt% peat to help obtain equal volumes of the growing media and to improve soil porosity. The fourth growing media consisted of 1 kg dw peat, equivalent to 3 dm^3, but with no sand (100 wt% peat). The cation exchange capacity (CEC) and base saturation (BS) was calculated based on the ammonium acetate extraction method, see below.

2.2 Pot experiment

All pH measurements were performed in a 1:2.5 soil to H_2O suspension, equilibrated for a minimum of 24 hours, and then shaken and sedimented for another hour before determining the pH. With the aid of some initial batch experiments, the combination of carbonatite or dolomite applications to growth media were optimized to result in a pH range within 5 to 7. Samples of growth media were supplied with increasing concentrations of carbonatite or dolomite, and pH was determined several times over a time span of 16 days (data not shown). Amounts of dolomite and carbonatite were then selected based on the equally apparent pH levels at "pseudo-equilibrium," which was met after approximately 14 days. For 3 dm^3 pots filled with 5, 20 and 50 vol% peat, an application of 42 g dolomite (equal to the liming effect of approximately 100 g carbonatite) was sufficient, though pots filled with 100 vol% peat required 63 g dolomite (equal to the liming effect of approximately 150 g carbonatite) to reach an acceptable pH (Table 1). Pots filled with 20 and 50 vol% peat were also given an additional dose of 150 g carbonatite. Pots filled with 5 vol% peat were not treated with 150 g carbonatite rock powder, as the pH would then increase beyond >7.5. Selected amounts of dolomite and carbonatite were supplied to pots, and the humid growth media (60% of water holding capacity), including nutrients (see below), were equilibrated for 15 days. Then, 10 mL soil was sampled for pH determination seven days after sowing or prickling (Table 1). Again, after 14 weeks of root development, two samples of 10 mL from each pot (one at the top and one at the bottom) were collected for pH determination.

((Table 1))

Liquid fertilizers were initially applied to pots sown with tall fescue, corresponding to 300, 75 and 300 mg pot^{-1} of N ($Ca(NO_3)_2$), P ($Ca(H_2PO_4)$) and K (K_2SO_4), respectively. Seeds of white clover were inoculated with rhizobium bacteria by germinating them in 10 mL of rhizobia containing soil. After 10 days, seedlings were prickled to their respective pots, which had been supplied with N, P and K corresponding to 180, 75, and 300 mg pot^{-1}, respectively. In addition, all pots were given 25 mL each of $FeSO_4$ x 7 H_2O (5 g L^{-1}), $(NH_4)_6Mo_7O_{24}$ x 4 H_2O (0.05 g L^{-1}), $MnSO_4$ x1H_2O (2.5 g L^{-1}), $CuSO_4$ x 5 H_2O (2.5 g L^{-1}), $ZnSO_4$ x H_2O (1.5 g L^{-1}), $Na_2B_4O_7$ x 10 H_2O (0.25 g L^{-1}) and $MgSO_4$ x 7 H_2O (12.5 g L^{-1}). Precisely 12 seeds per pot of tall fescue and four seedlings of white clover per pot were grown in a greenhouse. After six and 10 weeks (first and second harvest, respectively), the pots received an additional supply of NPK, but with some exceptions: pots containing carbonatite were not applied with any additional K, whereas pots grown with white clover were not applied with any additional N. Each treatment was conducted in four replicates. The pot experiment was conducted under environmentally controlled conditions at 19±1 ºC during the day (16h) and 15±1 ºC at night (8h), with an approximate photon flux of 200 µmol m^{-2} s^{-1} during the daytime. The humidity of growth media was maintained near 60% of water-holding capacity by weighing each pot every second day, and supplying MilliQ-H_2O (conductive resistance >18 MΩ cm^{-1}) throughout the entire experimental period. All reagents used were of analytical grade or better, and all water was deionized MilliQ-H_2O.

2.3 Soil and plant analysis

The Ba concentration in peat was determined by ICP-MS analysis (Agilent 8800 Triple Quadrupole) after the digestion of approximately 0.180 g of accurately weighed material in nitric acid (69 wt% HNO_3, sub-boiled ultrapure) using a microwave technique (Milestone UltraClave 3; hold time 25 minutes at the maximum temperature 250 ºC). The Ba, Sr, Ca, Mg and K concentrations in the sand, dolomite and carbonatite rock powder (Table 2) were determined by ICP-MS analysis after HNO_3 digestion of approximately 0.250 g of accurately weighed homogenized material using a microwave technique. The concentration of soil organic carbon (C) (Table 2) was determined using a LECO TruSpec analyzer. The exchangeable concentrations of Ca, Mg, Na and K (Table 1) were determined in 3.00 g of dried growth media (2 mm) after extraction with 25 mL of 1M NH_4-acetate at pH 7.0 (*Schollenberger and Simon*, 1945; *Hesse and Muray*, 1971) .

((Table 2))

Shoots of tall fescue and trifoliate leaves of white clover were harvested 6, 10 and 14 weeks after germination. Plants samples were pooled in one sample per pot, and subsequently dried at 50°C for 72 h, before the weighing and determination of the dry matter yield. Dry plant samples were then milled, and approximately 0.200 g of accurately weighed plant material was digested in 69 wt% HNO_3 (sub-boiled ultrapure) using a microwave technique (Milestone UltraClave 3, hold time 25 minutes at the maximum temperature of 250 ºC). The concentrations of Ba, Ca, K, Mg, molybdenum (Mo), P, sulphur (S), copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) were determined using ICP-MS, although here we present only the Ba, Sr, Ca, Mg and K concentrations.

Accuracy was checked by a simultaneous analysis of certified reference materials: NCS 85113, GBW 07603 CRM Trace elements in food, NCS ZC 73013 Spinach, International Atomic Energy Agency (IAEA) V-10 Hay, NIST 1515 Apple leaves, NIST 1575 Pine needles, NIST 1570a Trace Elements in Spinach, NIST 2709a San Joaquin Soil and NIST 2711a Montana II Soil. Our data was in accordance with the certified or recommended values issued. Intermediate precision (within-laboratory reproducibility; n = 4) reflected variations associated with, e.g. nonhomogeneous growth medium.

2.4 Statistics

A principal component analysis (PCA) was performed using JMP Pro 12. A factorial regression analysis, ANOVA, correlation matrix, student's T-test and Tukey's familywise test were also carried out using the software $R_{x64\ 3.2.2}$, and $R_{commander}$ (*Faraway*, 2002).

3 Results

3.1 Characteristics of the growth media

Dolomite and carbonatite were mixed with peat in combinations to ensure that the pH was within an acceptable range for optimal plant growth. No significant difference in pH at the top and bottom of each pot was detected by the end of the trial period (t-tests, $p > 0.05$). Although not statistically significant for all separate treatment combinations, a general increase in pH from the start to the end within each treatment in the pot experiment was evident (Fig. 1). At the end of the experiment, pH was buffered between 6 and 7 in pots grown with tall fescue treated with dolomite, irrespective of the peat content in the pots. In all other pots, the increasing content of peat forced the pH down. Even in the dolomite-treated pots grown with white clover, the peat effect was stronger, and the pH was reduced (Tukey's tests, $p<0.05$, Fig. 1). The initial pH is given less attention, as the mineral applications apparently require some time to equilibrate with peat. Compared to 150 g carbonatite, the 63 g dolomite treatment seemed to buffer the pH more effectively in the presence of white clover (T-test, $p<0.05$) compared to tall fescue (T-test, $p=0.39$). Within each peat treatment, the 100 g carbonatite additions to white clover buffered the pH drop more effectively compared to the 42 g dolomite addition (T-tests, $p<0.05$, Fig. 1), although 42 g dolomite was estimated to equal the liming effect of 100 g carbonatite. The cation exchange capacity of the growth media increased with the addition of peat (Table 1).

((Figure 1))

3.2 Dry weight of plants

The plant dry weights (dw) are shown in Fig. 2, and we recorded a significant increase in dry weight from the first harvest compared to the second and third harvest (Tukey's test: $p < 0.001$). The dry weight harvests ranged from approximately 1 g (six weeks of growth) to approximately 7 g (14 weeks) per pot. Generally, the lowest yields were recorded for plants grown in 5 vol% peat, but no other significant effects of treatments or pH were noticed ($p > 0.05$).

((Figure 2))

3.3 Plant uptake

From now on, all element amounts taken up by plants are reported on a dry weight basis calculated as concentration multiplied by yield (total mg pot^{-1}). The total uptake of Ba, Sr, Ca, Mg and K in plants is provided in Fig. 2. A principal component analysis (PCA) was performed to investigate the variation in the uptake of Ba, Sr, Ca, Mg and K in plants as affected by two orthogonal principal components conditional to the experimental design. The resulting biplot displayed in Fig. 3 shows that the relationship between Ba, Sr and Ca uptake by plants is strongly related to the carbonatite rock powder-treated pots and with white clover, while the Mg uptake is more strongly related to the dolomite-treated pots and with tall fescue plants. Potassium, dry weight and weeks of harvest are all equally affected by both principal components, but in different directions (Fig. 3). Dry weight and weeks of growth are strongly related. The two principal components are also strongly affected by mineral treatment (comp. 1) and test plant (comp. 2). The different symbols used to label the observations confirm the impact of the mineral treatments and test crops used on the variation in observations quite visible.

((Figure 3))

The possible Ba enrichment in plants derived from carbonatite is of great concern; hence, a factorial regression model was applied to help analyse the effect of plant species (white clover and tall fescue), treatment (100 g carbonatite and 42 g dolomite) and peat gradient (5, 20 and 50 vol% peat) on Ba uptake (µg Ba pot^{-1}, log-normalized) for each harvest. Soil containing only peat does not contain sand, and flowingly no sand-derived Ba. These pots were therefore not included in the model. We found interactions between soil, species and treatment to be slightly significant ($p = 0.05$, Fig. 4d). Compared to dolomite, an additional increase in Ba uptake was noticed in pots treated with carbonatite ($p < 0.001$, Fig. 4c). Uptake of Ba in white clover was significantly higher compared to tall fescue ($p < 0.001$, Fig. 4a), while the Ba uptake was additionally increased with an increasing peat treatment ($p < 0.001$, Fig. 4b).

((Figure 4))

The ratio of K/(Ca + Mg) in plants grown on dolomite-treated pots was in the range from 1.2 to 5.6 in tall fescue and 1.1 to 2.4 in white clover. The similar rate in plants grown on carbonatite-treated pots ranged from 3.2 to 6.6 in tall fescue and from 1.5 to 2.1 in white clover. The median ratio for both treatments was 4.0 in tall fescue and 1.6 in white clover.

4 Discussion

4.1 Geochemical effects of the experimental design

Calcium in dolomite and Ca in carbonatite are bound in different minerals, and with a different geochemistry. The batch experiments showed that comparable doses of carbonatite required to equal the pH effect of dolomite, could be fairly well estimated by its fraction of calcite (≈ 42%). However, it can be seen in Fig. 1 that the carbonatite treatment raises the pH the most. Consequently, it is likely that the buffering potential of carbonatite during titration was underestimated when using pure water instead of a weak salt solution (e.g. 0.01M $CaCl_2$, *Eckert and Sims*, 2011). A higher ionic strength of the equilibrium solution could have dissolved the calcite from the carbonatite more effectively, thus resulting in less applied carbonatite to help balance the dolomite treatment. Moreover, the relative buffering capacity of carbonatite and dolomite both seem equal when white clover is grown (Fig. 1), as the fall in pH with an increasing vol% of peat is near equal. In pots grown with tall fescue, the dolomite buffers the pH well. The impact of the test crop on pH development in the dolomite-treated pots indicates that besides the geochemistry of the minerals applied, the root activity and plant factor also play a role. Compared to pots grown with tall fescue, the reduction of pH in the dolomite treated pots of white clover indicate a more active uptake regime, in one way or the other, and probably a higher biological activity in the rhizosphere. In general, the soil liming effect of dolomite and carbonatite is effective when weathering and the dissolution of these minerals takes place. The latter is possibly affected by the presence of organic acids, and uptake of mineral nutrients, the excretion of protons at the root surface and microbial activity. These are processes which amplify the weathering of minerals in the rhizosphere (Essington, 2004; *Rengel and Marschner*, 2005; *Dotaniya and Meena*, 2014). Thus, the biogeochemical processes can be measured indirectly as changes in pH over time, and in this trial the pH generally increased from the start towards the termination of the pot experiment (Fig. 1) within each treatment combination. This is interpreted as an indication of carbonatite and dolomite weathering during the trial period. In Fig. 3 it can be seen that the pH, yield (indicated as dry weight) and growth period (weeks) are all strongly related, which exemplifies the close relationship between plants, rhizosphere and geochemistry in soil. Nonetheless, our results indicate that the yield itself is insignificantly affected by the use of either dolomite or carbonatite as a liming agent, for both tall fescue and white clover. It is the mineral uptake that is affected.

Barium in the sand substitutes K in the K-feldspar due to a similar ionic radius (*Heier*, 1962; *Shaw and Penczak*, 1996), and for that reason the Ba in sand was expected to be nearly unavailable to the test crops. Compared to Sr, in which the main contribution to plants is derived from carbonatite, our findings provided evidence that the sand in fact contributed with a considerable portion of Ba to plants. This is shown by the measured Ba uptake by plants treated with dolomite only (Fig. 2). *Myrvang* and co-authors (2016) also demonstrated Ba uptake from this particular sand to tall fescue and white clover in a previous work. Despite that the sand contains nearly 20 times more Ba than carbonatite, an additional contribution to plant Ba from carbonatite was still evident, as shown in Fig. 4c. According to Heim et al. (2012), Ba replaces up to 10% of the K sites in the crystal structure of biotite, while up to 90% of total Sr in carbonatite is bound within the calcite. Biotite serves as the primary source of available K in the applied carbonatite rock powder, and because biotite and calcite weather quite easily, Ba, K and Sr will be supplied to soil.

4.2 Mobility and uptake of Ba, Sr, Ca, Mg and K in the soil-plant system

Besides a fall in pH, peat-derived organic acids seem to have mobilized the investigated base cations, including Ba and Sr, thereby increasing their availability to plants (Fig. 2). This effect is strongest when comparing the Sr uptake in plants between vol% parts of peat-given carbonatite, as the main source to Sr in the growth media comes from the carbonatite (Table 2). Considering Ba uptake by the plants, the less predominant effect of 100 vol% peat as it appears in Fig. 2, is directly connected to the lack of Ba source derived from sand. High concentrations of soil organic matter are reported to adsorb Ba (*Madejón,* 2013). However, by calculating the enrichment factor for plant Ba derived from carbonatite within each growth medium (subtracting the Ba uptake in plants given carbonatite in Fig. 2 from the Ba uptake in plants given dolomite, data not shown), a steady increase in Ba uptake from 5 to 100 vol%

peat is discovered, thus exemplifying that Ba might still be relatively mobile in soil (*Kabata-Pendias*, 2011). *Lamb* and colleagues (2013) reported a significantly positive relationship between the plant uptake of Ba and Ba adsorbed to soil colloids derived from ion exchange sites in soil. As demonstrated in our experiment, the ability of tall fescue and white clover in taking up Ba and Sr seems to overcome the Ba adsorption potential of peat. Results from a speciation study connected to this experiment provide evidence which suggests that Ba mobilizes from both the sand and carbonatite rock powder to exchangeable sites on peat and colloids, which in turn is made available to plants (unpublished data).

The results in Fig. 2 show a higher uptake of Ba, Sr and Ca in white clover compared to tall fescue. As early as 1950, *Robinson* and colleagues (1950) reported that some leguminous species, such as alfalfa and soybean, tended to accumulate relatively large quantities of Ba compared to wheat and corn grain. According to *Loneragan and Snowball* (1969), a higher requirement for Ca by legumes compared to grasses is evident. Compared to tall fescue, the higher Ba and Ca uptake by white clover (Fig. 2), and the close relationship between these two elements (Fig. 3), agrees well with findings reported by *Myrvang* et al. (2016), who reported that white clover accumulated these elements more effectively than tall fescue. The close relationship between Ba, Sr and Ca (Fig. 3) also supports findings from a vegetation study on carbonatite soil at Stjernøy (*Myrvang* et al., submitted), in which a significant correlation between Ba and Ca, and Sr and Ca in the 23 indigenous plants studied has been reported. This is likely controlled by uptake mechanisms in plants (e.g. *Cipollini and Pickering*, 1986; *Mitra*, 2015), since plants may exert an influence on the actual uptake of an element by the selective absorption of cations (*Gjengedal* et al., 2015; *Collander*, 1941), but which also results from a similar geochemistry between these ions (*Kabata-Pendias*, 2011; *Marschner*, 2012).

As can be seen in Fig. 2, the uptake of K exceeded the amount of K added as soluble fertilizer (300 mg pot^{-1}) in pots treated with carbonatite. Hence, a large portion of the plant K derives from the carbonatite. Compared to the total of 900 mg of soluble K applied to pots treated with dolomite only, plants grown on carbonatite suppled with an additional 300 mg of soluble K, took up even more K. It is not clear why tall fescue and white clover accumulated more K from pots treated with carbonatite, since the soluble K added to dolomite pots was more than sufficient compared to the plant's requirements. However, the high Mg uptake to plants given dolomite compared to plants given carbonatite may indicate an antagonistic effect of Mg on K uptake (*Jefferson* et al., 2001; *Yara*, 2015). The total amount of soluble Mg added (30 mg Mg pot^{-1}) was less than the total Mg uptake (up to 100 mg pot^{-1}). This indicates that carbonatite-Mg also adds to the source of Mg taken up by the plants. Dolomite was indeed a significantly larger source to plant Mg than carbonatite (Figs. 2 and 3), which is natural due to its composition (Table 2). The ratio of K/(Ca + Mg) is an important quality parameter in fodder crops (the rate should ideally be less than 2.2, *Jefferson* et al., 2001). Here, the increased Ca supply from carbonatite and/or dolomite seems to compensate for an insufficient supply of Mg to maintain an ideal plant rate of these cations in white clover. Considering tall fescue, an elevated K to Ca+Mg ratio (> 2.2) apparent for both liming agents is related to the lower Ca uptake. For this reason, there is no evidence to suggest any increased imbalance in the relationship between K, Mg and Ca by substituting dolomite with carbonatite, although field trials would be useful to investigate possible losses resulting from climate-derived processes such as run-off and leaching.

This study was not designed to test the phytotoxicity of Ba, as toxic symptoms may occur internally in the plants long before the plant yield is affected (e.g. *Llugany* et al., 2000). Still, the plant concentrations of Ba observed are well below concentrations reported to cause internal toxicity symptoms, such as the Ba blocking of K channels in soybeans (*Llugany* et al., 2000) and Tanzanian guinea grass (*Monteiro* et al., 2011). Compared to uptakes reported in *Myrvang* et al. (2016), the relatively low uptake of Ba in tall fescue and white clover is possibly related to Ba precipitation with sulfate (*Kabata-Pendias*, 2011) applied as nutrient solutions. This observation is also interesting when evaluating the differences in growth conditions in field trials and in a pot experiment. The plants sampled at Stjernøy (*Myrvang* et al., submitted) grew directly on rocks that had been weathered since the last Ice Age (8000-9000 years ago), whereas plants grown in pots had been exposed to the same rock only recently broken up and grinded. As a result, those newly exposed rock surfaces had only been exposed to a weathering process for a very short time in comparison. This has very likely solubilized less plant-available Ba to plants grown in the pot experiment, despite the plants in a pot experiment exploring a small volume of the growth media more effectively compared to being grown in field trials.

5 Conclusion

The pot experiment was designed to test the liming effect of carbonatite compared to dolomite, as well as the potential impact on yield and the uptake of Ba, Sr, Ca, Mg and K to tall fescue and white clover on an increasing supply of peat. Compared to dolomite, the pH effect of carbonatite exhibited a higher relative variability by increasing peat content; nevertheless, the plant dry weight was not significantly affected. Compared to pots given dolomite and soluble K, the uptake of K from carbonatite to plants was equally high or higher, and thus, highly available to the test crops. Carbonatite was a significant source of plant Ba and Sr, with these elements primarily following the Ca uptake. The uptake of Ba, Sr, Ca, Mg and K to plants was further increased by an additional supply of peat to the growth medium, probably due to an organic acid-induced weathering of carbonatite. White clover concentrated Ba, Sr and Ca to significantly higher concentrations than tall fescue. Even so, the Ba and Sr concentrations in plants were relatively moderate compared to plant concentrations commonly reported. The pot experiment indicates that carbonatite may be used as a lime with additional K; however, caution needs to be addressed to soils with high contents of organic acids, and plants with a particular acquisition for Ca, as Ba and Sr uptake may be amplified. Compared to dolomite-treated pots, no additional imbalance in the K/(Mg+Ca) ratio in plants was observed when using carbonatite, but the generally high nutrient uptakes should stimulate field trials, as e.g. climatic factors, and nutrient leaching and runoff may influence the nutrient balance.

6 References

Bakken, A. K., Gautneb, H., Myhr, K. (1997): The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. *Nutr. Cycl. Agroecosyst.* 47, 41-48.

Bakken, A. K., Gautneb, H., Sveistrup, T., Myhr, K. (2000): Crushed rocks and mine tailings applied as K fertilizers on grassland. *Nutr. Cycl. Agroecosyst.* 56, 53-57.

Cipollini, M. L., Pickering, J. L. (1986): Determination of the phytotoxicity of barium in leach-field disposal of gas well brines. *Plant Soil* 92, 159-169.

Collander, R. (1941): Selective absorption of cations by higher plants. *Plant Physiol.* 4, 691-720.

Dotaniya, M. K., Meena, V. D. (2014): Rhizosphere effect on nutrient availability in soil and its uptake by plants: A review. *Proceedings of the National Academy of Science, India Section B: Biological Sciences*. 85 (1), 1-12.

Eckert, D., Sims, J. T. (2011): Recommended soil pH and Lime Requirement tests. Chapter 3 in: Recommended Soil Testing Procedures for the Northeastern United States, 3rd Ed. In: Northeastern Regional Bulletin. No. 493.

Essington, M. E. (2004): Soil and Water Chemistry - An Integrated Approach. CRC Press LLC. p. 534.

Faraway, J. J. (2002): Practical Regression and Anova using R. Available at: www.stat.lsa.umich.edu/˜faraway/book.

Gautneb, H. (2009): Review of the geology and the apatite distribution of the carbonatite in the Lillebukt Alkaline Comples, Stjernøy Northern Norway. *Geol. Surv. Norway,* Report no. 2009.061.1-35.

Gjengedal, E., Martinsen, T., Steinnes, E. (2015): Background levels of some major, trace, and rare earth elements in indigenous plant species growing in Norway and the influence of soil acidification, soil parent material, and seasonal variation on these levels. *Environ. Monit. Assess.* 187, 1-28

Heier, K. S. (1962): Trace elements in feldspars - a review. *Norsk Geol. Tidsskr.* 42, 415-454.

Heim, M. (2001): Norsk steinmel til (øko-)landbruk: historikk, status quo, utfordringer og muligheter. In: *Sammendr. Nord. Mineralsymp. "Verdiskapning fra mineral til ferdig produkt".* Trondheim, April 2001, 16-22.

Heim, M., Hillersøy, M. H., Bleken, M. A., Gautneb, H., Gjengedal, E. (2012): Apatite-biotite-carbonatite (Stjernøy, N-Norway) - potential and obstacles regarding a multinutrient rock-fertilizer. *10th Int. Congr. Appl. Mineral. (ICAM)*, 327-334.

Hesse, P. R., Muray, J. (1971): A textbook of soil chemical analysis, pp. 91-105.

Jefferson, P. G., Mayland, H. F., Asay, K. H., Berdahl, J. D. (2001): Plant genetic resources. Variation in mineral concentration and grass tetany potential among Russian wildrye accessions. *Crop Sci.* 41, 543-548.

Kabata-Pendias, A. (2011): Trace Elements in Soils and Plants. Fourth edition. *Taylor and Francis Group*. pp. 142-144.

Lamb, D. T., Matanitobua, V. P., Palanisami, T., Megharaj, M, Naidu, R. (2013): Bioavailability of barium to plants and invertebrates in soil contaminated by barite. *Environ. Sci. Techn.* 47, 4670-4676.

Llugany, M., Poschenrieder, C., Barceló, J. (2000): Assessment of barium toxicity in bush beans. *Arch. Environ. Contam. Toxicol.* 39, 440-444.

Loneragan, T. J., Snowball, K. (1969): Calcium requirements of plants. *Aust. J. agric. Res.* 20, 465-477.

Madejón, P. (2013): Barium, in: Alloway, B. J.: Heavy Metals in Soils - Trace Metals and Metalloids in Soils and their Bioavailability. Third Edition. Environmental Pollution. Springer 22. pp. 507-513.

Marschner, P. (2012): Mineral Nutrition of Higher Plants Third Edition. School Agric. Food Wine. Univ. Adelaide. Australia. pp. 25-28.

Mitra, G. N. (2015): Calcium. 54. In: Regulation of Nutrient Uptake by Plants - A Biochemical and Molecular Approach. Dept. Soil Sci. Agric. Chem., Orisa University of Agriculture and Technology, India. p. 54.

Monteiro, F. A., Nogueirol, R. C., Melo, L. C. A., Artur, A. G., Rocha, F. (2011): Effect of barium on growth and macronutrient nutrition in Tanzania guinea grass grown in nutrient solution. *Commun. Soil Sci. Plant Anal.* 42, 1510-1520.

Myrvang, M. B., Bleken, M. A., Krogstad, T., Heim, M. Gjengedal, E. (2016a): Can liming reduce barium uptake by agricultural plants grown on sandy soil? *J. Plant Nutr. Soil Sci.* 27. 179, 557-565.

Myrvang, M. B., Hillersøy, M. H., Heim, M., Bleken, M. A., Gjengedal, E.: Uptake of macronutrients, barium, and strontium to vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway. Submitted to *J. Plant Nutr. Soil Sci*. July, 2016.

Rengel, Z., Marschner, P. (2005): Nutrient availability and management in the rhizosphere: Exploiting genotypic differences. *New Phytol.* 168 (2); 305-312.

Robinson, W. O., Whetstone, R. R., Ergington, G. (1950): The occurrence of barium in soils and plants. *U.S. Dept. Agric. Techn. Bull.* 1013, 1-36.

Shaw, C. S. J., Penczak, R. S. (1996): Barium and titanium-rich biotite and phlogopite from the western and eastern Gabbro, Coldwell alkaline complex, northwestern Ontario. *Canadian Mineral.* 34, 967-975.

Schollenberger, C. J., Simon, R. H. (1945): Determination of exchange capacity and exchangeable bases in soil. Ammonium acetate method. *Soil Sci.* 59, 13-24.

Strand, T (1981): Lillebukt alkaline kompleks; karbonatittens mineralogi og petrokjemi. Cand. real. thesis, University of Bergen, 287 pp. (In Norwegian).

Table 1: Selected properties of the growth media given sodium hydroxide (NaOH, control), dolomite (D) or carbonatite (C). Barium and macronutrients are determined in solution after extraction with 1M ammonium acetate at pH 7.

Peat vol%	Treatment (g/pot)	Sand (g/ pot)	Peat (g/ pot)	pH Tall fescue	pH White clover	Ba (cmol_+/kg)	Ca (cmol_+/kg)	Mg (cmol_+/kg)	K (cmol_+/kg)	CEC[a] (cmol_+/kg)	BS[b] (%)	Total C (%)	Porosity[c] (ϕ)
5	0_{control}	2 100	50	4.2	4.4	0.032	0.35	0.12	<0.079[e]	3.6	13	1.2	0.20
5	42_{D}	2 100	50	6.4	6.7	0.030	2.5	0.58	<0.024[d]	3.5	88	1.4	0.20
5	100_{C}	2 100	50	7.6	7.2	0.042	8.5	0.15	<0.079[e]	8.7	100	1.3	0.20
20	42_{D}	2 100	200	5.5	6.1	0.031	3.5	1.3	<0.024[d]	5.6	85	4.5	0.24
20	100_{C}	2 100	200	6.2	6.7	0.044	9.7	0.35	<0.079[e]	10	100	4.4	0.24
20	150_{C}	2 100	200	6.7	7.0	0.046	13	0.36	<0.079[e]	13	100	4.4	0.24
50	42_{D}	2 100	500	5.2	5.9	0.039	7.2	4.2	<0.079[e]	16	70	9.7	0.26
50	100_{C}	2 100	500	5.6	5.7	0.043	12	0.6	<0.079[e]	14	94	9.5	0.26
50	150_{C}	2 100	500	5.5	6.4	0.044	15	0.5	<0.079[e]	16	100	9.4	0.26
100	63_{D}	0	1 000	4.7	5.8	0.009	54	38	<0.079[e]	120	77	48	0.37
100	100_{C}	0	1 000	4.5	4.9	0.074	84	7.0	<0.079[e]	110	80	46	0.37
100	150_{C}	0	1 000	5.0	5.1	0.078	84	5.2	<0.079[e]	100	88	44	0.37

[a] Cation exchange capacity (CEC) = the sum of Ca, Mg, K, Na and H (soil extraction with 1M ammonium acetate pH 7). [b] Base saturation (BS) was calculated as the 'base' cation percentage fraction of CEC. [c] Porosity equals the effective pore water fraction of the total bulk volume of the soil. [d] LOD: limit of detection. [e] LOQ: limit of quantification.

Table 2: Nitric acid extracted concentrations of selected elements (mg kg^{-1}), and pH (equilibrated for 24 h) in each component of the growth media (g kg^{-1}).

	Sand (n=8)	Peat (n=4)	Dolomite (n=4)	Carbonatite (n=6)	Polystyrene balls
Ba	0.35±0.012	3.8±0.10	0.012±0.0022	2.4±0.40	-
Sr	0.043±0.0045	-	0.120±0	3.9±0.67	-
Ca	2.4±0.45	-	230±5	200±30	-
Mg	0.54±0.082	-	130±0	23±4.5	-
K	19.6±0.48	-	<LOD	26±5.7	-
pH	4.7^{a}	3.8^{a}	9.5^{a}	9.3^{a}	-
Weight (1 dm^{3}) g	1 400	330	-	-	51

LOD: limit of detection, - : not measured, a superscript: n=1.

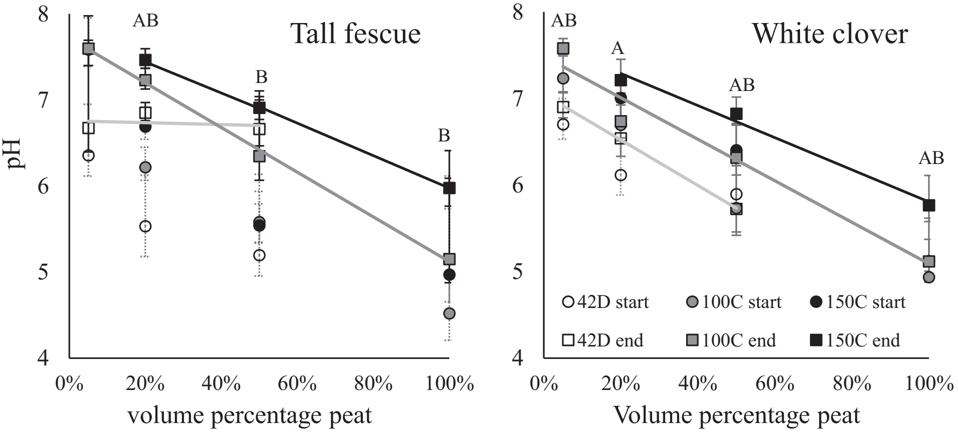
Figure Captions:

Figure 1: Mean pH ±SD in pots of tall fescue and white clover at the start and at the end of the pot experiment. The trend lines are connecting equal mineral treatments with pH observations at the end of the experiment. 42D = 42 dolomite pot^{-1}. 100C and 150C = 100 and 150 g carbonatite pot^{-1}. A significant difference in pH ($p<0.05$) resulting from carbonatite treatment compared to the apparent equal liming effect caused by dolomite within each growth media is indicated with the upper-case letter A. A significant increase in pH ($p<0.05$) within each treatment and growth media from start to end of the pot experiment is indicated by upper-case letter B on the top of the end-pH columns. Statistics are performed by two sample t-test (95% confidence level, CL).

Figure 2: Dry weight (DW) of plant samples. Uptake of Mg, K, Ca, Sr and Ba in: a) tall fescue and b) white clover after harvesting at 6, 10 and 14 weeks. 42D and 63D = 42 and 63 g dolomite. 100C and 150C = 100 and 150 g carbonatite. The element concentration (g kg^{-1}) can be obtained by dividing the element uptake (mg pot^{-1}) by DW (g).

Figure 3: Biplot giving the influence of element concentration, pH, dry weight (DW), weeks of harvest and peat organic matter. Triangles represent carbonatite, and circles represent dolomite. The cluster of points is related to interactions between harvests, species, peat and treatment on element uptake. Encircled symbols top right include white clover, and encircled symbols bottom left include tall fescue.

Figure 4: Effect plot for interactions between harvest and: **a)** species, **b**) soil and **c**) treatment in response to log normalized Ba content (µg/pot); **d)** Interaction between species, soil and treatment. Bars represent the pooled coefficient of variance (CV) equal to the square root of MSE obtained from the ANOVA table (table not shown). 42D = 42 g dolomite added to each pot, 100C = 100 g carbonatite added to each pot.



Tall fescue
White clover
pH
8
7
6
5
4
0%
20%
40%
60%
80%
100%
volume percentage peat
Volume percentage peat
AB
B
B
AB
A
AB
AB
○42D start
●100C start
●150C start
□42D end
■100C end
■150C end

Figure 1

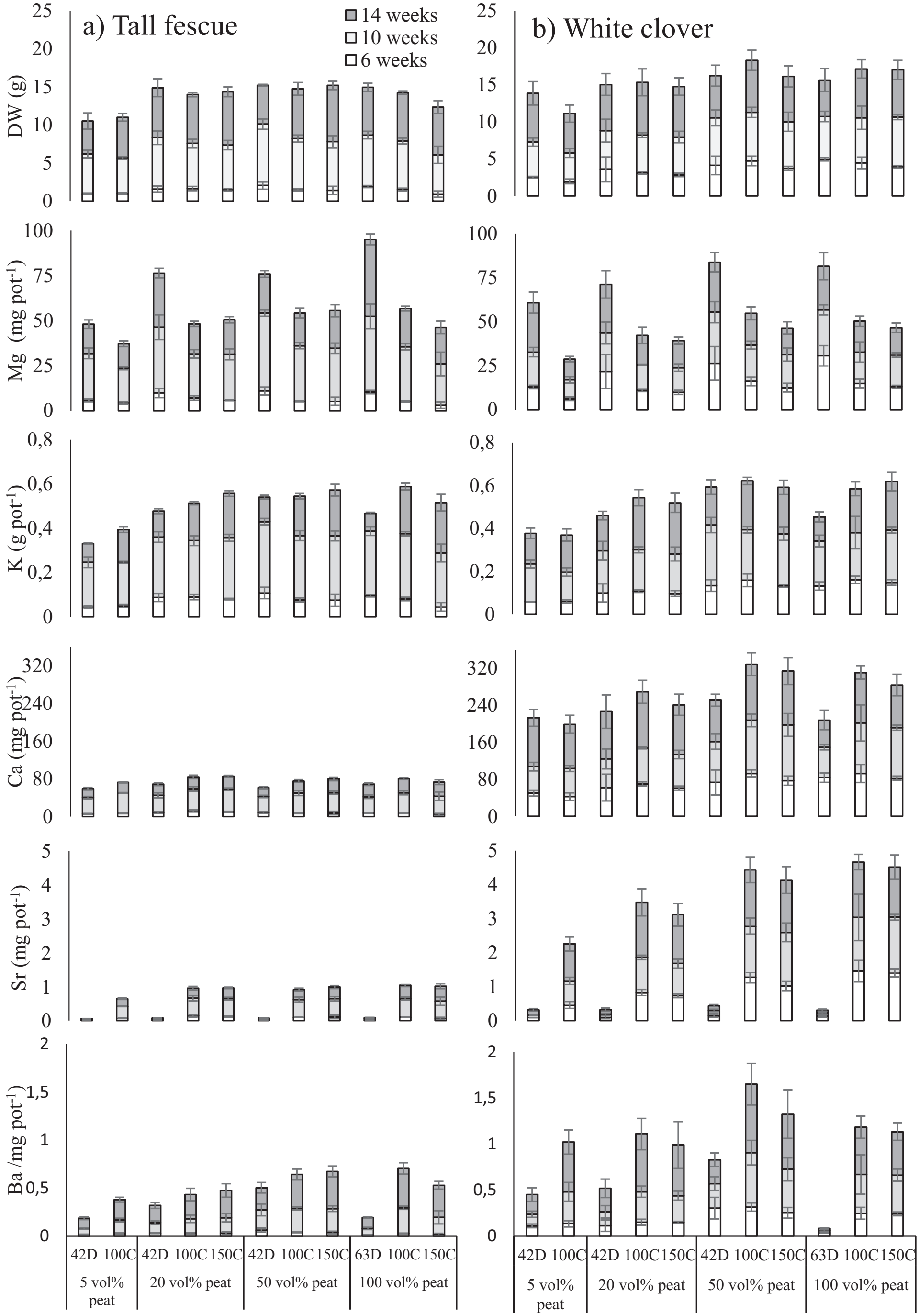

a) Tall fescue
b) White clover
▨ 14 weeks
☐ 10 weeks
☐ 6 weeks
DW (g)
0
5
10
15
20
25
Mg (mg pot^{-1})
0
25
50
75
100
K (g pot^{-1})
0
0,2
0,4
0,6
0,8
Ca (mg pot^{-1})
0
80
160
240
320
Sr (mg pot^{-1})
0
1
2
3
4
5
Ba /mg pot^{-1})
0
0,5
1
1,5
2
42D
100C
42D
100C
150C
42D
100C
150C
63D
100C
150C
5 vol% peat
20 vol% peat
50 vol% peat
100 vol% peat

Figure 2

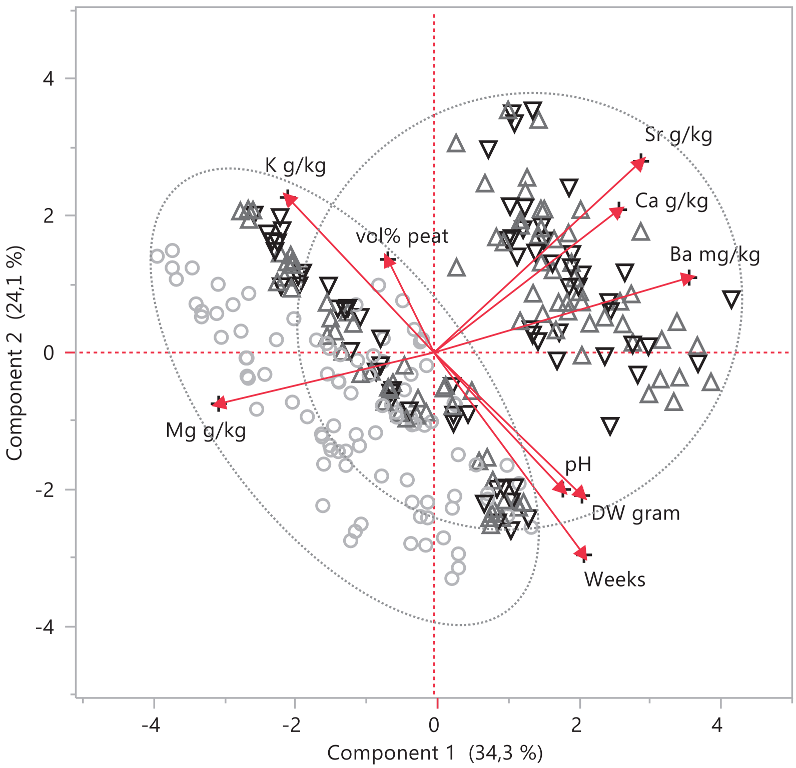

Component 2 (24,1 %)
Component 1 (34,3 %)
4
2
0
-2
-4
-4
-2
0
2
4
Sr g/kg
K g/kg
Ca g/kg
vol% peat
Ba mg/kg
Mg g/kg
pH
DW gram
Weeks

Figure 3

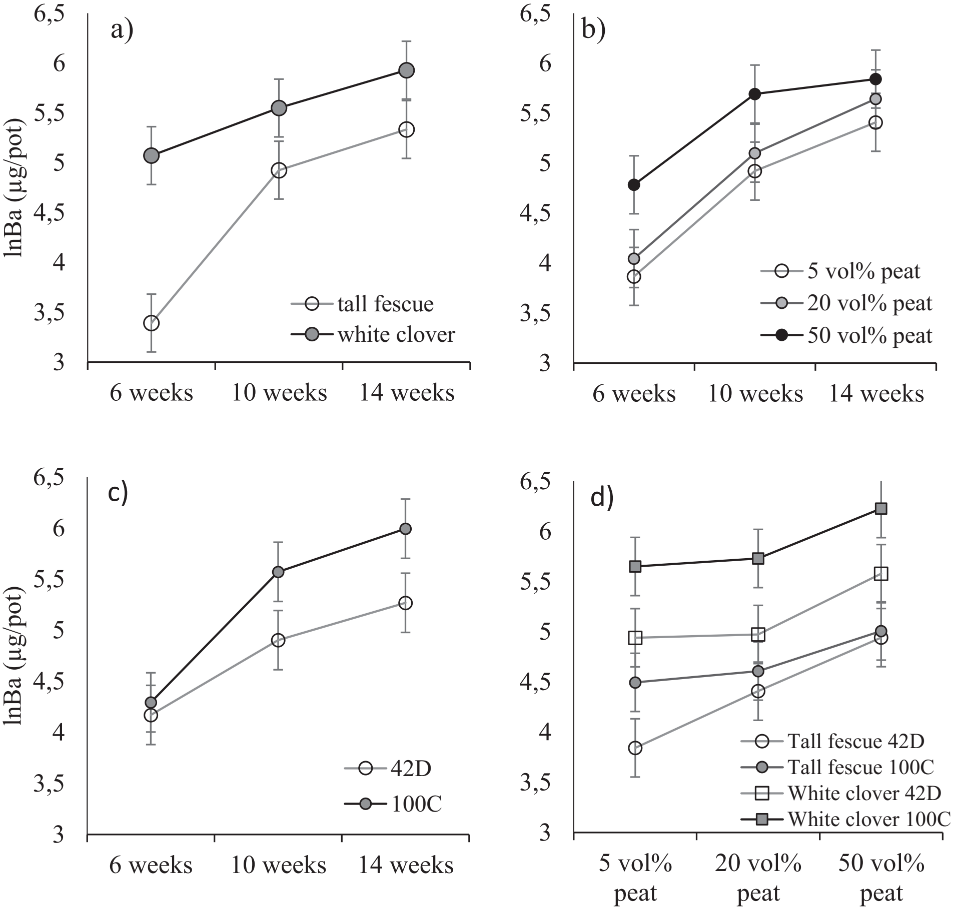

a)
b)
c)
d)
lnBa (µg/pot)
6,5
6
5,5
5
4,5
4
3,5
3
6 weeks
10 weeks
14 weeks
tall fescue
white clover
5 vol% peat
20 vol% peat
50 vol% peat
42D
100C
Tall fescue 42D
Tall fescue 100C
White clover 42D
White clover 100C
5 vol% peat
20 vol% peat
50 vol% peat

Figure 4

Paper IV

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Geochemistry of barium in soils supplied with carbonatite rock powder and barium uptake to plants☆

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ABSTRACT

Apatite-biotite-carbonatite (short form: carbonatite) rock powder originating from Lillebukt alkaline complex, N-Norway is a potential liming and multi-nutrient fertilizer. However, the elevated contents of potentially bio-toxic barium (Ba) (up to 5.5 g kg^{-1}) is a matter of concern. A pot experiment was conducted in order to investigate the geochemistry of Ba in a sandy peat-containing growth media treated with carbonatite, with special focus on Ba-speciation in the pore water. These results were correlated with Ba uptake in *Trifolium repens* L. (white clover) and *Fesctua arundinácea* L. (tall fescue). The Ba-speciation and bioavailability as affected by treatment and plant growth was conducted using WHAM/Model VI version 7.0.4 and the diffusive gradients in thin films (DGT) technique, respectively. The increasing cation exchange capacity (CEC) in the growth media, and colloidal fulvic acids (FA) decreased the Ba^{2+} concentration in pore water. Both the Ba detected in DGT (Ba_{dgt}), and exchangeable Ba (Ba_{exc}) were higher in pots containing rock powder. A strong relationship between Ba_{exc} and diffusively bound Ba to FA (Ba_{dfa}) with plant uptake was evident. The latter was likely initiated by organic material mobilization of Ba from carbonatite. The mobilized Ba bound to FA (Ba_{fa}) in pore water was mainly bound diffusively, and the Ba_{dfa} fraction was thus made available to plants. Finally, the Ba_{dgt} was increased in pots grown with white clover compared to tall fescue. Further investigation is required to determine if this is related to increased rhizosphere activity by plants or to the nitrogen fixating plant-microbe relationship.

1. Introduction

In recent years the use of crushed rocks and minerals as soil amendment in farming practices has received increased attention (Van Straaten, 2006). In addition to its liming potential, the minerals in rock powder weather over time, sustaining steady supply of macro- and micro-nutrients to plants. The carbonatite rock from the Lillebukt alkaline complex, located at Stjernøy in the Northern part of Norway (70° 17.75′ N, 22° 34.5′ E), contains substantial amounts of calcite (~40% $CaCO_3$), K (2.7% K, mainly in biotite), phosphorus (2.0% P in apatite) and magnesium (2.7% Mg, mainly in biotite) (Heim et al., 2012). Bakken et al., (1997, 2000), reported K to be easily weathered from the biotite fraction, which in turn was available to plants grown in carbonatite-rock treated soils. However, the potentially hazardous element barium (Ba) can substitute K in the sheet interlayers of biotite (Shaw and Penczak, 1996) and hence pose undesired Ba-uptake when applying this mineral in agroecosystems. In the carbonatite rock from Stjernøy, Ba replaces up to 10% of K sites in biotite. Since Ba follows the geochemical fate of K due to similar ionic radius (Kabata-Pendias, 2011), Ba may be released to soil in considerable amounts. The fate of K in the soil system and its availability to plants under different conditions has been examined closely (e.g. Marschner, 1993). The exchangeable and free K ions in soil and pore water are easily absorbed by plant roots. Barium on the other hand, may exchange other cations and precipitate in soil and pore water as oxides and hydroxides (Kabata-Pendias, 2011), or in the presence of sulfates and carbonates (Choudhury and Cary, 2001). The use of barium chloride ($BaCl_2$) method for determination of soil CEC has been adopted by the American Society of Agronomy (Gillman and Sumpter, 1986), due to the Ba's ability to exchange other cations in soil. A field study at Stjernøy comprising 23 native plant species grown in mineral soil developed on carbonatite bedrock, showed that all species were able to take up Ba from the soil. Exceptionally high concentrations of Ba (up to 2 g Ba kg^{-1} dry weight plant material) in *Vicia cracca* L.

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0883-2927/

(bird vetch) were reported (Myrvang et al., 2016a). Studies on Ba uptake by plants show that some species are able to accumulate high concentrations of Ba (Choudhury and Cary, 2001; Kabata-Pendias, 2011). These findings suggest that Ba can be highly mobile and available to plants grown in Ba-rich soils. The literature reports considerable progress in recent years on speciation of trace elements, their mobility and transport as well as the associated ecological risks (Almås et al., 2007; Almås et al., 2006; Degryse et al., 2009; Ivezic et al., 2013; Lofts et al., 2004; Mason et al., 2013; Nolan et al., 2005; Okkenhaug et al., 2015; Zhang and Davison, 2015), still the biogeochemistry of Ba in soil is not equally well investigated. A study on a barite contaminated area reported indications of increased Ba mobility when adsorbed to organic substances in water extracts (Lagas et al., 1984). Lamb et al. (2013) suggested that Ba in pore water was supplied from cation exchange sites associated with surface of soil colloids and thus supplied Ba to plant roots.

Based on earlier findings connected to this study (not yet published), we hypothesize that (i) Ba bioavailability is controlled by the free ion activity of Ba in pore water and lability species on mineral surfaces; (ii) Ba adsorbed to dissolved humic substances will be mobile in soil, and therefore more available to plants; (iii) the release of Ba from carbonatite to soil will increase by supply of peat organic matter. To test the three hypothesis, we conducted a pot experiment with test crops (*Festuca arundinácea* L. and *Trifolium repens* L.) grown in a sand mixed with carbonatite rock powder and added different amounts of peat. The WHAM/Model VI (version 7.0.4) was used to calculate the Ba^{2+} concentration and other Ba species in pore water before sowing, and DGT technique was used to estimate the *in situ* bioavailable metal concentration in pots containing the same soils as affected by rhizosphere activity.

2. Methods and materials

2.1. Characteristics of the growth media used in the pot experiment

The primary growth medium was an aeolian sand (0.06–0.6 mm) with a low content of total carbon (0.015 wt%). The sand composition is mainly quartz and feldspar originating from weathering of arkosic and granitic bedrock, where Ba is supposed to replace K and Ca in the non-exchangeable silica lattice of feldspars (Heier, 1962). Total Ba concentration (X-ray Fluorescence-analysis) in the sand and carbonatite was 500 ± 5 mg kg^{-1}, and 2500 ± 110 mg kg^{-1}, respectively. The concentrations of Ba in peat (3.8 ± 1 mg kg^{-1}) and dolomite (9.4 ± 0.51 mg kg^{-1}) was determined by means of ICP-OES (Perkin Elmer Optima 5300DV) after digestion in concentrated nitric acid (65 wt% sub-boiled ultra-pure HNO_3) using microwave technique (Milestone UltraClave 3; hold time 25 min at the maximum temperature 250 °C). The content of organic C was determined using a LECO TruSpec analyzer (Table 1). The pH in a soil-water suspension (1:2.5) was determined by means of a Thermo Scientific Orion2Star pH benchtop pH meter and a combined glass membrane electrode. Cation exchange capacity (CEC) and exchangeable Ba (Ba_{exc}) were measured by extracting 3.00 g dry soil in 25 mL 1 M ammonium acetate pH 7.0 for 24 h followed by filtration through blue ribbon filter. Metal concentrations were determined by means of ICP-OES, and CEC was calculated as the sum of protons, K, sodium (Na), Ca, and Mg (Tables 1 and 2). Reagents of analytical grade or better were used throughout, and all water used was de-ionized (>18 MΩ cm^{-1}).

2.2. Pot experiment

Trifolium repens L. (white clover) and *Festuca arundacea* L. (tall fescue) (Lid and Lid, 1998) were cultivated in a greenhouse experiment. Initially 2.1 kg dry matter (DM) of sand were mixed with 50, 200, and 500 g, respectively, of unfertilized peat DM (equal to about 2, 10, and 20 wt% peat per pot) in 3 dm^{-3} non-perforated pots. Porosity was improved in pots of 2 and 10 wt% peat by adding inert polystyrene balls adjusting to a total soil volume of 3 dm^3. The fourth growth medium consisted of 1000 g peat DM equivalent to 3 dm^3. The pH was optimized to range within 5–7 in all the pots. Sand and peat mixes that were not supplied with carbonatite, were supplied with dolomite to an equal lime effect (Table 2). In the control pots (Table 2), 50 mL of 0.075 M NaOH was supplied to increase pH. Sand mixed with 2 wt% was not given 150 g carbonatite, as the pH would increase beyond 7.5. Thereafter liquid fertilizers were applied to treatments grown with tall fescue, corresponding to 300, 75, and 300 mg pot^{-1} of N, P, and K, respectively. The white clover cultivated pots were added liquid fertilizers corresponding to 180, 75, and 300 mg pot^{-1} of N, P, and K, respectively. Initially seeds of white clover were germinated in a 10 mL soil naturally containing rhizobium bacteria for inoculation, and seedlings were prickled to their respective pots. Per pot, 12 seeds of tall fescue and 4 seedlings of white clover were applied. Each treatment was conducted with four replicates. Plants were grown under environmentally controlled conditions with a temperature at 19 ± 1 °C during day (16 h) and 15 ± 1 °C at night (8 h). In order to simulate day light, 500 W lamps emitting yellow and white light in equal intensity, with an approximate photon flux of 200 μmol m^{-2} s^{-1} at day time, were used. The soil humidity was kept near 60% of the potential water holding capacity by measuring total weight every second day. Weight of each pot was balanced by deionized water throughout the experimental period.

2.3. Plant harvest and analysis

Leaves and stem of tall fescue and trifoliate leaves of white clover were harvested at 6, 10, and 14 weeks after sowing. Plant samples were dried at 50 °C for 72 h before recording the DM yield. Subsequently, plant samples were milled, and approximately 0.2 g accurately weighed samples were digested at 250 °C (25 min at maximum temperature) with 65 wt% HNO_3 (sub-boiled ultrapure), using microwave technique. The plant concentrations of Ba in addition to aluminium (Al), Ca, K, Mg, sodium (Na), sulfur (S), and iron (Fe) were determined using ICP-MS (Agilent 8800 Triple Quadrupole).

Table 1
Selected properties (mean and standard deviation, n = 3) of carbonatite, dolomite, aeolean sand and unfertilized peat before application.

	pH_{H2O}	CEC (cmol+ kg^{-1})	BS (%)	Total C (%)	Exchangeable Ba (cmol+ kg^{-1})
Carbonatite	9.3[a]	65 ± 5.4	100	4.5 ± 0.23	0.13 ± 0.011
Dolomite	9.5[a]	38.7 ± 0.95	100	12.56 ± 0.070	0.0014 ± 0.00011
Aeolean sand	4.7[a]	0.51 ± 0.024	100	0.015 ± 0.0028	0.0310 ± 0.00045
Unfertilized peat	3.8[a]	126 ± 1.8	9.5 ± 0.35	50.8 ± 0.37	0.0093 ± 0.00075

[a] n = 1.

Table 2
Selected properties of each growth media supplied with either dolomite of carbonatite in each 3L pot before sowing.

Peat fraction	pH_{H2O}	Dry weight of growth media	CEC	BS	Total C	Porosity	Total Ba in pots (tot-Ba_{pot})	Ba concentration in pots	Ba_{exc} concentration in pots	Fraction Ba_{exc} (mg pot^{-1}) of tot-Ba_{pot} (mg pot^{-1})
(wt%)	(n = 9)	(kg pot^{-1})	($cmol^+ kg^{-1}$)	(%)	(wv%)	Φ	(mg pot^{-1})	(mg kg^{-1})	($cmol^+ kg^{-1}$)	(%)
$2_{control}$	4.3 ± 0.2	2.17	3.6	13.1	1,2	0.20	1100	480	0.032	4.5
2_{D42}	6.6 ± 0.3	2.22	3.5	88.1	1.4	0.20	1100	470	0.030	4.3
2_{C100}	7.4 ± 0.3	2.27	8.7	100	1.3	0.20	1300	570	0.042	5.0
10_{D42}	6.0 ± 0.5	2.36	5.6	85.2	4.5	0.24	1100	450	0.031	4.8
10_{C100}	6.5 ± 0.3	2.42	10.1	100	4.4	0.24	1300	540	0.044	5.6
10_{C150}	6.8 ± 0.3	2.47	13.4	100	4.4	0.24	1400	580	0.046	5.4
20_{D42}	5.6 ± 0.4	2.64	16.4	69.5	9.7	0.26	1100	400	0.039	6.7
20_{C100}	5.7 ± 0.5	2.70	13.4	93.8	9.5	0.26	1300	480	0.043	6.1
20_{C150}	6.0 ± 0.5	2.75	15.5	100	9.4	0.26	1400	520	0.044	5.8
100_{D63}	5.3 ± 0.6	1.06	120	77.1	48.1	0.37	4.4	4.1	0.009	100
100_{C100}	4.9 ± 0.3	1.10	114	80.0	46.2	0.37	260	240	0.074	22
100_{C150}	5.3 ± 0.4	1.15	101	88.1	44.4	0.37	380	330	0.078	16

Control = 50 mL 0.075 M NaOH added to the control pot. D42 and D63 = 42 and 63 g dolomite added to the respective pot. C100 and C150 = 100 and 150 g carbonatite added to the respective pot.
Porosity less than 0.26 in the growth media were improved by adding polystyrene balls equal to a total pot volume of 3 dm^3.
Tot-Ba_{pot} (mg pot^{-1}): The sum of Ba (sand analyzed by X-ray fluorescence, and nitric acid digested peat, dolomite and rock powder quantified by ICP-OES) of the respective 3 dm^3 pot.
Ba concentration in pots (mg kg^{-1}) = Tot-Ba_{pot} divided by the respective dry weight of the growth media.
BS = base saturation calculated as the fraction of base cations of CEC. Exchangeable Ba (Ba_{exc}) = ammonium acetate pH 7 extraction.

2.4. Deployment of DGT

Diffusive Gradient in Thin films (DGT) disks were provided by the DGT-Research (www.dgtresearch.com). These DGT disks were supplied with a Chelex resin for the accumulation of labile Ba in pore water, and labile Ba replenished from geochemically active binding sites in the growth media during deployment time. The DGT-disks were deployed in twelve pots grown with tall fescue, and twelve pots grown with white clover. Likewise conducted by Almås et al. (2006), each DGT disk was inserted carefully in the top soil one week before the first harvest. For each plant species the pots deployed with DGT were randomly chosen among replicates for each factor combination. Additionally one set of DGT-disks were deployed in each pot replicate (4 replicates) of one treatment combination to test replicate variability. Temperature was recorded during the 48 h deployment time. Then the disks were removed and rinsed with deionized water before dismantling. The resins were eluted with 65 wt% sub-boiled ultra-pure HNO_3, and the eluates were diluted with de-ionized water before analysis. Concentrations of Ba in the final eluates were determined by the ICP-MS.

2.5. Pore water sampling

Twelve pore water samples were collected all together, one from each growth media and treatment combination provided in the pot experiment. These samples were initially collected from “undisturbed” soils, i.e. without rhizosphere impact from plant growth. Clean and unused 200 mL plastic pots were equipped with mesh-slits in the bottom, prior to filling with soil. Soil samples were brought to field capacity with de-ionized water, as in Almås et al. (2006). The pots were then wrapped in elastic plastic film and left in room temperature for 2 days equilibration. The equilibrated pore water was displaced by carefully adding de-ionized water in aliquots equivalent to the estimated pore volume at the top. To ensure all equilibrated water was recovered, vacuum was applied and the equilibrated water was collected at the bottom directly into clean and unused test tubes. The collected water samples were filtered through 0.45 μm membrane filters and transferred to a new set of test tubes (HDPE quality provided by vwr.com) prior to pH determination (Table 3). Then, the leachates were conserved by adding 0.5 mL of ethylene diamine tetra acetic acid (EDTA) to 4.5 mL leachate, to prevent precipitation pending analysis. The concentration of a number of elements (Table 3) in the equilibrated water, from now on coined pore water (PW), were determined by ICP-MS. The concentration of dissolved organic carbon (DOC) in soil water extracts were determined by a Shimadzu TOC-5000 analyzer after shaking 4 g soil in 40 mL distilled water for 24 h. Only 2 g soil was used for soils containing 100% peat. Ideally, this parameter should have been measured in the same pore water as evacuated from the pots, but DOC was not measured then, and had to be obtained later since it is an essential parameter for speciation calculations (Almås et al., 2007). The extracts were immediately after passed through a 0.45 μm micro pore filters (vwr.com) before analysis. Before modelling, the DOC concentrations were recalculated to equal the liquid to solution ratio of the pore water.

2.6. WHAM modelling

The speciation of Ba in pore water was calculated using WHAM/Model VI version 7.0.4 for waters. Input parameters are provided in Table 3. Likewise Almås et al., (2006), dissolved organic matter (DOM) estimated through the determination of DOC in soil water extracts, was assumed to have the ion-binding properties of “default” fulvic acid (FA), as defined in WHAM/Model VI. Fulvic acid was calculated to consist of 50% carbon by weight. Moreover, 50% of the acid groups of FA were suggested to be active in proton/metal binding. In such a pot experiment, dissolved Fe was assumed to be dominated by FeIII. The WHAM data base is available for WHAM users.

2.7. Statistics

Regression analyses, ANOVA, correlation matrix and T-tests were carried out using the software $R_{x64\ 301}$, and $R_{commander}$ (Faraway, 2002).

3. Results

3.1. Speciation of Ba in soil and pore water

Among the individual soil components applied, the peat was the dominating contributor to the CEC, while the carbonatite provided

Table 3
Element concentration in pore water.

Peat fraction	pH	DOC	S	Al_{tot}	Fe_{tot}	Ca	K	Mg	Na	Ba
(wt%)		(mg L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})
$2_{control}$	4.3	36	0.034	$3.60 \cdot 10^{-3}$	$2.69 \cdot 10^{-3}$	$7.98 \cdot 10^{-3}$	0.024	0.0049	0.17	$3.50 \cdot 10^{-4}$
2_{D42}	6.6	58	0.078	$1.78 \cdot 10^{-3}$	$1.45 \cdot 10^{-3}$	1.42	0.11	1.10	0.25	$6.26 \cdot 10^{-3}$
2_{C100}	7.5	60	0.131	$1.52 \cdot 10^{-2}$	$1.29 \cdot 10^{-2}$	0.80	0.17	0.14	0.19	$3.20 \cdot 10^{-3}$
10_{D42}	5.9	120	0.109	$4.82 \cdot 10^{-3}$	$4.48 \cdot 10^{-3}$	1.05	0.061	1.03	0.24	$3.06 \cdot 10^{-3}$
10_{C100}	6.7	190	0.212	$2.45 \cdot 10^{-3}$	$2.69 \cdot 10^{-3}$	2.35	0.18	0.38	0.33	$5.46 \cdot 10^{-3}$
10_{C150}	6.7	120	0.115	$6.67 \cdot 10^{-3}$	$7.34 \cdot 10^{-3}$	0.62	0.14	0.086	0.16	$1.60 \cdot 10^{-3}$
20_{D42}	5.4	400	0.14	$1.04 \cdot 10^{-2}$	$8.59 \cdot 10^{-3}$	0.77	0.069	0.82	0.26	$1.89 \cdot 10^{-3}$
20_{C100}	5.6	290	0.243	$2.22 \cdot 10^{-2}$	$2.15 \cdot 10^{-2}$	0.77	0.12	0.16	0.30	$2.04 \cdot 10^{-3}$
20_{C150}	6.0	250	0.262	$4.08 \cdot 10^{-3}$	$4.30 \cdot 10^{-3}$	1.80	0.092	0.27	0.32	$2.99 \cdot 10^{-3}$
100_{D63}	5.3	3860	0.072	$4.82 \cdot 10^{-3}$	$5.37 \cdot 10^{-3}$	0.20	0.021	0.28	0.15	$2.77 \cdot 10^{-4}$
100_{C100}	5.0	2500	0.14	$4.08 \cdot 10^{-3}$	$6.09 \cdot 10^{-3}$	0.47	0.033	0.12	0.22	$3.20 \cdot 10^{-4}$
100_{C150}	5.5	2190	0.115	$3.45 \cdot 10^{-3}$	$6.09 \cdot 10^{-3}$	0.97	0.044	0.13	0.19	$5.32 \cdot 10^{-4}$

Control = 50 mL 0.075 M NaOH. D42 and D63 = 42 and 63 g dolomite added to the respective pot, respectively. C100 and C150 = 100 and 150 g carbonatite added to the respective pot, respectively.

the highest exchangeable Ba (Ba_{exc}) concentration (Table 1). The total content of Ba in the different treatments (tot-Ba_{pot}; sum of Ba in carbonatite-rock, sand, and peat), and some other important chemical characteristics have been calculated, and these are shown in Table 2. The resulting concentration of Ba_{exc} is very much at the same level among the dolomite and carbonatite treated pots. Looking upon all the different treatment material combinations, the concentration of dissolved organic carbon (DOC) in PW showed a strong linear relationship with both the tot-C ($r^2 = 0.94$, $n = 12$, $p < 0.001$) and with the CEC ($r^2 = 0.94$, $n = 12$, $p < 0.001$). Pore water concentrations of Ca, Mg, K, and Na (Table 3) co-correlated all with total concentration of Ba in PW (Ba_{pw}, $p < 0.001$). The free Ca^{2+} concentration (Ca was the most abundant cation in PW) showed a positive linear relationship with the free Ba^{2+} concentration ($F_{16} = 62$, $r^2 = 81\%$. $P < 0.001$, Fig. 1c). The PW concentration of essential input parameters are shown in Table 3, and an extract of the resulting Ba speciation is given Table 4. The total S detected in pore water was measured by ICP-MS, and hence, we tested three speciation scenarios of its partitioning as SO_4^{2-} (100, 10 and 1% as SO_4^{2-} out of total S in PW). The only significant effect was a substantial reduction of the $BaSO_4^0$ concentrations (Table 4). The concentration of Ba^{2+} was insignificantly affected by the concentration of SO_4^{2-}, although the $BaSO_4^0$ concentrations exceeded the solubility product of $BaSO_4$ (with the exception of pots containing 100% peat), and hence, most of the dissolved S is probably organic (deriving from the peat) not available for precipitating $BaSO_4$. This assumption is supported by a significant and positive linear relationship between DOC and total S in pore water ($F_8 = 42$, $r^2 = 88\%$, $p < 0.001$). It is not unlikely that close to 100% of S is present in the organic matter, but since we cannot exclude the presence of SO_4^{2-}, results from the 1% scenario is reported for the remaining discussions on the fate of Ba-speciation in this experiment (Table 4).

The Ba^{2+} contributed from about 50 to 95% of Ba_{pw} in pots containing 2 to 20 wt% peat, and nothing in PW from the 100 wt% peat treatments. The most significant factors controlling immobilization of Ba^{2+} (log-normalized) in PW was the DOC in PW ($r^2 = 0.92$, $n = 12$, $p < 0.001$), and the CEC of soil (Fig. 1b: $r^2 = 0.97$, $n = 12$, $p < 0.001$). As the fraction of Ba_{pw} bound to colloidal FA (Ba_{fa}) increased, the Ba^{2+} concentration decreased (Fig. 1a: $r^2 = 0.85$, $n = 12$, $p < 0.001$).

The fraction of Ba bound to FA in PW (Ba_{fa}/Ba_{pw}) ranged from 4 to 100%, which was linearly related to the Tot-C content in the pots

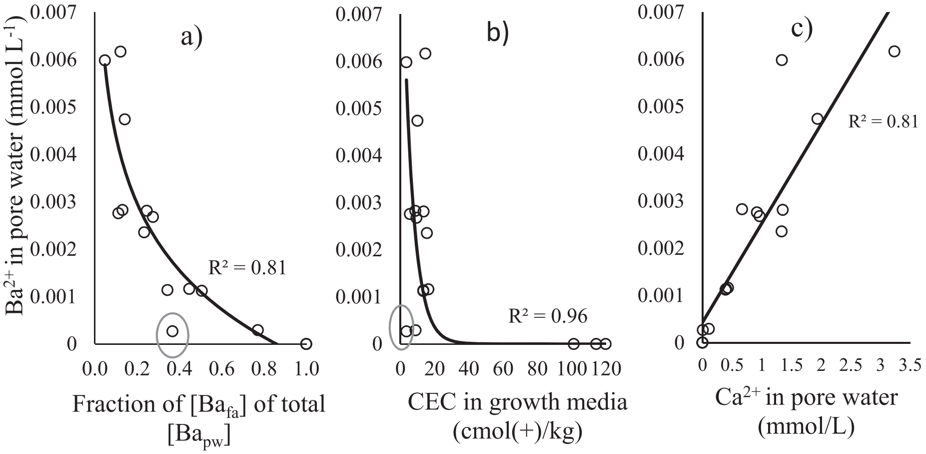

Fig. 1. Ba^{2+} concentration in pore water related to a) the fraction of Ba bound to colloidal fulvic acids in pore water (Ba_{fa}/Ba_{pw}), b) cation exchange capacity (CEC) of growth media, and c) Ca^{2+} concentration in pore water. The encircled points mark the sandy soil (control) without dolomite or carbonatite rock powder.

Table 4
Concentration of the most significant Ba compounds in pore water calculated by WHAM.

Peat fraction	$BaSO_4^0$ (100% S)	$BaSO_4^0$ (10% S)	$BaSO_4^0$ (1% S)	Ca^{2+}	Ba^{2+}	tot-Ba_{fa}	Diffusive Ba_{dfa}	Specifically Ba_{sfa}
(wt%)	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})	(mmol L^{-1})
$2_{control}$	$1.65 \cdot 10^{-6}$	$1.75 \cdot 10^{-7}$	$1.76 \cdot 10^{-8}$	$6.01 \cdot 10^{-3}$	$2.67 \cdot 10^{-4}$	$1.28 \cdot 10^{-4}$	$1.21 \cdot 10^{-4}$	$7.51 \cdot 10^{-6}$
2_{D42}	$3.48 \cdot 10^{-5}$	$3.50 \cdot 10^{-6}$	$3.50 \cdot 10^{-7}$	1.34	$5.98 \cdot 10^{-3}$	$2.97 \cdot 10^{-4}$	$1.66 \cdot 10^{-4}$	$1.31 \cdot 10^{-4}$
2_{C100}	$3.95 \cdot 10^{-5}$	$4.03 \cdot 10^{-6}$	$4.03 \cdot 10^{-7}$	$6.66 \cdot 10^{-1}$	$2.83 \cdot 10^{-3}$	$4.19 \cdot 10^{-4}$	$2.41 \cdot 10^{-4}$	$1.78 \cdot 10^{-4}$
10_{D42}	$2.51 \cdot 10^{-5}$	$2.54 \cdot 10^{-6}$	$2.54 \cdot 10^{-7}$	$9.17 \cdot 10^{-1}$	$2.76 \cdot 10^{-3}$	$3.40 \cdot 10^{-4}$	$2.10 \cdot 10^{-4}$	$1.31 \cdot 10^{-4}$
10_{C100}	$7.76 \cdot 10^{-5}$	$7.89 \cdot 10^{-6}$	$7.90 \cdot 10^{-7}$	1.94	$4.74 \cdot 10^{-3}$	$7.74 \cdot 10^{-4}$	$4.42 \cdot 10^{-4}$	$3.32 \cdot 10^{-4}$
10_{C150}	$1.67 \cdot 10^{-5}$	$1.72 \cdot 10^{-6}$	$1.72 \cdot 10^{-7}$	$3.97 \cdot 10^{-1}$	$1.14 \cdot 10^{-3}$	$5.50 \cdot 10^{-4}$	$3.47 \cdot 10^{-4}$	$2.03 \cdot 10^{-4}$
20_{D42}	$1.81 \cdot 10^{-5}$	$1.85 \cdot 10^{-6}$	$1.86 \cdot 10^{-7}$	$4.31 \cdot 10^{-1}$	$1.16 \cdot 10^{-3}$	$8.44 \cdot 10^{-4}$	$5.87 \cdot 10^{-4}$	$2.58 \cdot 10^{-4}$
20_{C100}	$3.55 \cdot 10^{-5}$	$3.75 \cdot 10^{-6}$	$3.78 \cdot 10^{-7}$	$3.89 \cdot 10^{-1}$	$1.12 \cdot 10^{-3}$	$1.03 \cdot 10^{-3}$	$7.50 \cdot 10^{-4}$	$2.80 \cdot 10^{-4}$
20_{C150}	$5.58 \cdot 10^{-5}$	$5.73 \cdot 10^{-6}$	$5.75 \cdot 10^{-7}$	1.33	$2.35 \cdot 10^{-3}$	$6.96 \cdot 10^{-4}$	$4.39 \cdot 10^{-4}$	$2.58 \cdot 10^{-4}$
100_{D63}	$2.44 \cdot 10^{-13}$	$2.93 \cdot 10^{-14}$	$3.14 \cdot 10^{-15}$	$1.18 \cdot 10^{-8}$	$1.64 \cdot 10^{-11}$	$2.77 \cdot 10^{-4}$	$2.77 \cdot 10^{-4}$	$8.41 \cdot 10^{-10}$
100_{C100}	$7.37 \cdot 10^{-12}$	$9.03 \cdot 10^{-13}$	$9.59 \cdot 10^{-14}$	$3.88 \cdot 10^{-7}$	$2.63 \cdot 10^{-10}$	$3.20 \cdot 10^{-4}$	$3.20 \cdot 10^{-4}$	$3.79 \cdot 10^{-9}$
100_{C150}	$1.53 \cdot 10^{-12}$	$1.98 \cdot 10^{-13}$	$2.19 \cdot 10^{-14}$	$1.20 \cdot 10^{-7}$	$6.55 \cdot 10^{-11}$	$5.32 \cdot 10^{-4}$	$5.32 \cdot 10^{-4}$	$2.27 \cdot 10^{-9}$

When 10% and 1% of total S in pore water are implemented into WHAM, only the calculated $BaSO_4^0$ is affected. Ba_{fa} is the concentration of total (tot-Ba_{fa}), specifically (Ba_{sfa}) or diffusive (Ba_{dfa}) bound Ba to fulvic acid, FA.
Control = 50 mL 0.075 M NaOH. D42 and D63 = 42 and 63 g dolomite added to each pot, respectively. C100 and C150 = 100 and 150 g carbonatite added to each pot, respectively.

($r^2 = 0.86$, $n = 12$, $p < 0.001$). Barium diffusively bound to FA (Ba_{dfa}) was the dominating fraction of Ba_{fa} in PW (Table 4). The fraction of Ba accumulated by the DGT (Ba_{dgt}) out of total Ba in pore water (Ba_{dgt}/Ba_{pw}) ranged from 0.2 to 3%, and from 1 to 5% in pots grown with tall fescue and white clover, respectively. The mean Ba_{dgt} in the pots (Table 5) grown with white clover were significantly higher compared to pots grown with tall fescue (Two-sample T-test, $p < 0.001$). The Ba_{dgt} in pots with tall fescue showed a weak linear relationship to Ba_{dfa} ($r^2 = 0.16$, $n = 12$, $p = 0.004$).

3.2. Plant uptake of Ba

Stepwise model selection was carried out on Ba fractions in soil (Ba_{exc} and Ba_{dgt}) and all the Ba species in PW calculated by WHAM (Tables 2–4) to find the best model predicting Ba uptake by plants (Ba_{upt} is the Ba concentration in plants; Ba_{plant} given in Table 5, multiplied by the plant's dry weight). Both the Ba_{exc} in the different pots, and the Ba_{dfa} correlated positively to Ba_{upt}, and these relationships were even stronger when investigating the pots containing 100 wt% peat separately (Fig. 2 a and b). The internal correlation between these two Ba-species ($r^2 = 61\%$) were not multicollinearly significant (Zaidonin and Yap, 2013), and hence, both Ba-species were considered to be significantly affecting the Ba_{upt}.

The solution pH was not well correlated with Ba species in PW nor with the Ba_{upt}. Nor was the relationship between the Ba_{dgt} and Ba_{upt} significant when testing for each plant species separately ($p > 0.5$). Independent of plant species, however, a significant positive relationship of the Ba_{dgt} to Ba_{upt} was observed (Fig. 2c, $F_{18} = 18$, $r^2 = 53\%$, $p < 0.001$). The addition of carbonatite rock powder increased Ba_{upt} (Fig. 3a and b), and an additional increase was observed by increasing the content of peat in soil. The potential phytoextraction of Ba by plants was calculated using the transfer factor (TF = Ba_{plant} (mg kg^{-1})/Ba_{exc} (mg kg^{-1})) (Table 5) (Chojnacka et al., 2004; Abreu et al., 2012), where the Ba_{exc} (mg kg^{-1}) is obtained from the Ba_{exc} ($cmol_+$ kg^{-1}) in Table 2. Provided that equilibrium conditions exist and no diffusional limitations diminish transportation of metals to roots, the metal concentration in soil is

Table 5
Effective Ba concentration measured *in situ* by diffusive gradients in thin films technique (DGT) for each plant species. Plant dry weight (DW) and plant concentration of Ba ($n = 4$). Transfer factor (TF) of Ba from growth media to plant.

Peat fraction	Tall fescue				White clover			
(wt%)	Ba_{dgt} (μg L^{-1})	DW_{plant} (g)	Ba_{plant} (mg kg^{-1})	TF	Ba_{dgt} (μg L^{-1})	DW_{plant} (g)	Ba_{plant} (mg kg^{-1})	TF
$2_{control}$	1.8	10 ± 1.0	19 ± 4.2	0.86	8.3	11 ± 1.2	18 ± 4.3	0.84
2_{D42}	2.0	11 ± 1.0	18 ± 2.8	0.88	7.2	14 ± 1.3	33 ± 1.9	1.58
2_{C100}	5.6	11 ± 0.6	35 ± 5.1	1.20	10.6	11 ± 0.5	92 ± 11.2	3.20
10_{D42}	2.0	15 ± 1.5	21 ± 1.8	1.00	6.7	15 ± 4.3	34 ± 7.9	1.60
10_{C100}	3.8	14 ± 0.7	31 ± 8.4	1.02	7.8	15 ± 1.7	72 ± 5.5	2.39
10_{C150}	3.6	14 ± 1.0	33 ± 6.4	1.04	5.6	15 ± 1.5	70 ± 11	2.11
20_{D42}	3.1	15 ± 1.1	33 ± 7.2	1.23	7.8	16 ± 1.8	52 ± 8.7	1.92
20_{C100}	4.1 ± 0.55[a]	15 ± 1.3	44 ± 3.5	1.48	9 ± 1.5[b]	18 ± 2.0	90 ± 7.1	3.04
20_{C150}	3.8	15 ± 0.8	45 ± 7.0	1.47	10.0	16 ± 2.5	80 ± 13	2.70
100_{D63}	<1.2	15 ± 0.4	13 ± 1.1	2.08	<1.2	16 ± 1.7	5 ± 0.7	0.85
100_{C100}	2.3	14 ± 0.5	50 ± 5.4	0.69	2.1	17 ± 1.8	70 ± 16	1.35
100_{C150}	1.5	12 ± 0.9	43 ± 5.0	0.79	–	17 ± 1.2	67 ± 6.4	1.25

Transfer factor (TF) is total plant concentration (mg kg^{-1}) divided by the exchangeable concentration of Ba in growth media (mg kg^{-1}).
Control = 50 mL 0.075 M NaOH. D42 and D63 = 42 and 63 g dolomite added to each pot, respectively. C100 and C150 = 100 and 150 g carbonatite added to each pot, respectively.
Ba_{plant} is the mean Ba concentration in plants from the three harvests (6, 10 and 14 weeks).

[a] $n = 4$.

[b] $n = 3$. Ba_{dgt} is the concentration of Ba measured in the DGT-devices.

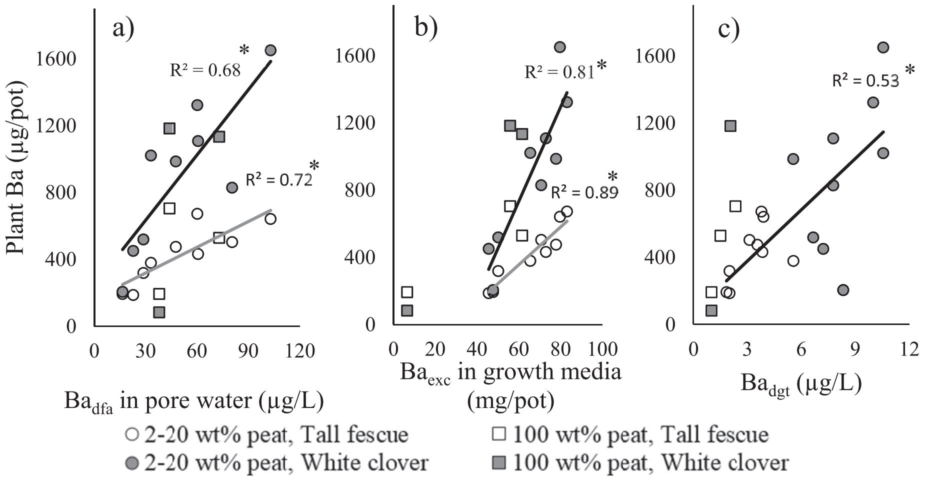

Fig. 2. Plant uptake of Ba related to a) exchangeable Ba (Ba_{exc}) in growth media, b) Ba diffusively bound to colloidal fulvic acids (Ba_{dfa}), and c) Ba concentration in the DGT-devices (Ba_{dgt}). Asterisks (*) indicate level of statistical significance >99%. Plants grown in 100% peat are not included in the regression model.

linearly transferred into the plant until uptake maxima (I_{max}) is reached (Degryse et al., 2009). The TF's shows that a significant portion of the Ba_{exc} in soil is readily available to plants.

The Ba_{exc} originating from carbonatite only (contribution from sand eliminated), was positively correlated to the respective plant uptake of Ba (Fig. 4).

4. Discussion

4.1. Mobilization of Ba in soil and pore water

The observations in this pot experiment indicate that the plant uptake of Ba was mainly controlled by the exchangeable Ba-fraction in the pots, in addition to the Ba weakly bound to dissolved organic matter (DOM, -coined fulvic acids in speciation calculations) in the pore water. The significance of soil organic matter (SOM) in binding Ba^{2+} agrees with findings in the current literature, reporting increased sorption of Ba in soils with high CEC (Madejón, 2010). In our experiment, CEC was mostly controlled by SOM, and Lee et al. (2007) reported that muscovite, particularly when coated with FA, showed great sorption capacity for Ba. The Ba ion in $BaCl_2$-FA solutions acted as a bridging cation between the muscovite and DOM (Lee et al., 2007). Although Ba is easily adsorbed by SOM, as well as by oxides and hydroxides, it can be relatively mobile in soils, particularly in acid ones (Kabata-Pendias, 2011). This is probably connected to the fact that Ba primarily binds to soil particles by ion exchange (Menzie et al., 2008; Zhang et al., 2001), and, although Ba is known to have a high affinity for SOM, such complexes are not very strong (Smith et al., 2004). Electrostatic forces account for a large fraction of the sorption of Ba on soil and subsoil, and the retention of Ba, like that of other alkaline earth cations, is largely controlled by the CEC of the sorbent (Choudhury and Cary, 2001).

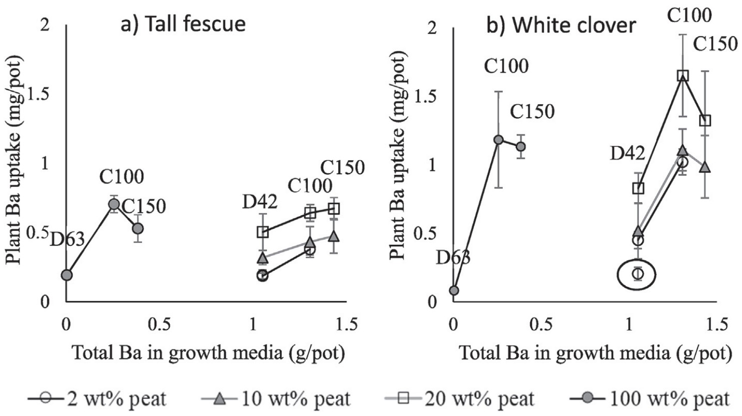

Fig. 3. Plant Ba uptake (mg/pot) in a) tall fescue and b) white clover related to total content of Ba in growth media (XRF-analysis of sand and carbonatite, and nitric acid extractable Ba in peat and dolomite). D42 and D63 = 42 and 63 g dolomite added to the growth media. C100 and C150 = 100 and 150 g carbonatite rock powder added to the growth media. Encircled point is the sandy soil (control without dolomite or carbonatite).

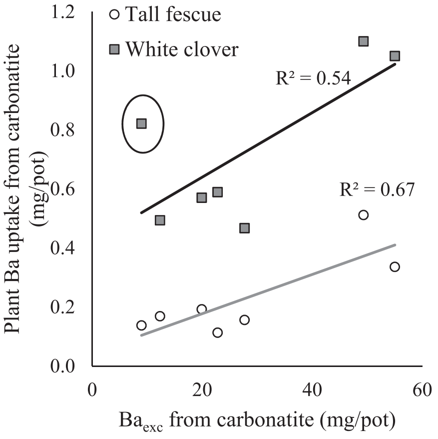

Fig. 4. Relationship between the exchangeable fraction of Ba in growth media derived from carbonatite, where the contribution of Ba from sand is eliminated, and the respective plant uptake. Circle marks the high plant uptake in growth media containing 20 wt% peat supplied with 100 g carbonatite.

Leaching experiments indicate that the formation of soluble organic Ba complexes from domestic wastes can contribute to Ba mobility in soils (Lagas et al., 1984). Barium substitutes K in the sheet interlayers of biotite (Heim et al., 2012; Shaw and Penczak, 1996), nevertheless the biotite mineral weathers quite easily, accordingly, Ba might be easily mobilized in soils where biotite is present in considerable amounts.

It is not clear why the Ba_{dgt} was not well correlated with the exchangeable Ba in the different growth media or with Ba^{2+} in PW. Garmo et al. (2003) reported that the DGT method was less suitable for some elements such as Ba, Fe, and Sr. Firstly, this could be related to a lower selectivity of the Chelex-100 resin for these elements at certain pH conditions. The mass of elements accumulated by the DGT-device is the time integrated sum of free ionic and labile metals in pore water, in addition to labile metals liberated as a response to the shift in solution equilibrium caused by uptake in the DGT (Zhang and Davison, 2015; Oliviera et al., 2012). Secondly, the DGT's are individually exposed in the pots, and hence some geochemical heterogeneity is observed (Table 5). These DGT's were also installed in pots cultivated with plants, and plant root activity might have increased the Ba heterogeneity in the growth media due to rhizosphere activity. The pore water was collected after saturating the growth media without plants, and hence is the recovered water an extract of the whole growth media volume (200 mL) not affected by plants. Thus the variation in Ba_{dgt} conditional to a small soil volume immediately in contact with the DGT, whereas the $Ba_{pw,}$ and hence the Ba^{2+}, indirectly mirrors the geochemistry of a larger volume of the growth media, this time without impacts of plants. A correlation test on the lognormal Ba_{dgt} concentrations with the sum of Ba_{dfa} plus Ba^{2+} provided a somewhat better correlation (pots grown with; tall fescue: $r^2 = 0.32$, $p = 0.03$; white clover: $r^2 = 0.45$, $p = 0.02$). Although the Ba_{dgt} was not strongly correlated with uptake when the test was plant species specific, the concentrations of Ba_{dgt} was substantially higher in pots grown with white clover compared to pots grown with tall fescue. This indicates an active plant factor in the rhizosphere of white clover, mobilizing more Ba from growth media components. The experiment was not designed to test possible microbial impact at the rhizosphere, hence it is unclear whether the increased Ba_{dgt} in the rhizosphere of white clover is connected to an increased microbial activity (Coscione and Berton, 2009), or whether this is simply connected to the fact that white clover is a dicot plant.

The tot-Ba_{pot} increases with the carbonatite contents in pots. However, by comparing the Ba_{exc} within the different treatments (carbonatite compared with dolomite), we can see that the differences in Ba_{exc} are small (Table 2). The other significant source of Ba is not dolomite or peat, but the sand (see "$2_{control}$", Table 2). This Ba derives from the feldspar which originally was expected to be geochemically inactive. However, our analyses showed this Ba to be exchangeable indeed. In pots containing 100 wt% peat (no sand), the difference between Ba_{exc} in pots given carbonatite is clearly higher compared with pots treated with dolomite.

4.2. Availability of Ba in growth media and uptake to plants

Plants cultivated in 100 wt% peat gained Ba primarily from carbonatite, and the transfer factor (Table 5) showed that a significant portion of the exchangeable Ba (Ba_{exc}) was taken up by plants. The Ba uptake in plants observed in control pots is suggested to derive mainly from the less soluble feldspar fraction in the sand. There is a limited number of studies on mechanisms controlling plant uptake of Ba from non-exchangeable sites in soil. An earlier experiment related to the present work (Myrvang et al., 2016b) showed that legumes were able to take up Ba from K-feldspar sand in concentrations of about 700 mg kg^{-1}, given low soil CEC and low ability for nutrient adsorption by soil. Other experiments have shown that even in fertilized soils, with sufficient supply of K, plants can extract and take up near 20% of the K from non-exchangeable sites, like the interlayer of clay (Marschner, 1993). We suggest this might also be the case for Ba, since Ba follows K in geochemical processes (Kabata-Pendias, 2011). The exchangeable Ba in the growth media was determined not withdrawn from the pot experiment, thus rhizosphere induced mobilization of Ba to exchangeable sites was not considered in the transfer calculations (TF) of Ba from soil to plant. The increased TF of Ba to white clover compared to tall fescue, indicated a higher capacity for white clover to extract Ba from pots amended with carbonatite rock powder. The increased Ba_{dgt} in pots of white clover, strengthens the hypothesis that white clover mobilize mineral bound Ba in the same manner as previously seen happening with K. In general, plant species with a high potential for root CEC may accumulate Ba in higher amounts than other species (Cipollini and Pickering, 1986).

All alkaline earth elements are absorbed by plants in the ionic form (He et al., 2012). The binding of Ba^{2+} to organic matter does not necessarily mean that Ba^{2+} is unavailable to plants. The main fraction of Ba_{fa}, which was diffusively bound, may supply Ba and other cations to the pore water-root interface. There is evidence to suggest that Ba in pore water originates mainly from cation exchange sites on colloids associated with biotite, and to a lesser extent K-feldspar, which in turn supply Ba to plant roots. These findings support the hypothesis of a colloid born Ba supply to roots from exchange sites in the growth media, in agreement with suggestions proposed by Lamb et al. (2013). The strong linear relationship between Ba_{pw} and the base cations, particularly the correlation between Ca^{2+} and Ba^{2+} (Fig. 1c), confirms that Ba follows the geochemistry, and flowingly competing for the same binding sites on organic matter and root surfaces, as the alkaline and alkaline earth metals. This correlation pattern was also demonstrated by Myrvang et al. (2016a), in a study of 23 native plant species grown on carbonatite mineral soil collected at Stjernøy.

5. Conclusion

A combination of increased cation exchange capacity in the different growth media, and the presence of colloids, induced a decrease in Ba^{2+} concentration in pore water. Thus, the first hypothesis of the bioavailability of Ba being controlled by all the labile Ba species in pore water, could not be confirmed. However, as the Ba^{2+} concentration in pore water decreased, the exchangeable fraction of Ba in the growth media increased by additional supply of both peat organic matter and carbonatite rock powder. Such peat amendments proved to enhance weakly bound colloidal Ba in the pore water, increasing the amount of available Ba to plants, and thereby confirming our second and third hypothesis. The investigated plant species took up its Ba mainly from the exchangeable fractions of the growth media, and Ba diffusively bound to colloids in pore water. Moreover, white clover mobilized Ba more effectively from the growth media than tall fescue, which increased the Ba uptake in comparison. The increased DGT-available Ba in pots containing white clover call for further investigation on rhizosphere activity, and possible microbial impact on the mobilization of Ba compounds in soils.

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References

Abreu, C.A., Cantoni, M., Coscione, A.R., Paz-Ferreiro, J., 2012. Organic matter and barium absorption by plant species grown in an area polluted with scrap metal residue. Appl. Environ. Soil Sci. 2012, 7. http://dx.doi.org/10.1155/2012/476821.

Almås, Å.R., Lofts, S., Mulder, J., Tipping, E., 2007. Solubility of major cations and Cu, Zn and Cd in soil extracts of some contaminated agricultural soils near a zinc smelter in Norway: modelling with a multisurface extension of WHAM. Eur. J. *Soil Sci.* 58, 1074–1086. http://dx.doi.org/10.1111/j.1365-2389.2007.00894.x.

Almås, Å.R., Lombnæs, P., Sogn, T.A., Mulder, J., 2006. Speciation of Cd and Zn in contaminated soils determined by DGT-DIFS, and WHAM Model/VI in relation to uptake by spinach and ryegrass. Chemosphere 62, 1647–1655. http://dx.doi.org/10.1016/j.chemosphere.2005.06.020.

Bakken, A.K., Gautneb, H., Myhr, K., 1997. The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. Nutr. Cycl. Agroecosyst. 47, 8. http://dx.doi.org/10.1007/BF01985717.

Bakken, A.K., Gautneb, H., Sveistrup, T., Myhr, K., 2000. Crushed rocks and mine tailings applied as K fertilizers on grassland. Nutr. Cycl. Agroecosyst 56. http://dx.doi.org/10.1023/A:1009709914578.

Chojnacka, K., Chonjacki, A., Górecka, H., Górecki, H., 2004. Bioavailability of heavy metals from polluted soils to plants. Sci. Tot. Environ. 337, 175. http://dx.doi.org/10.1016/j.scitotenv.2004.06.009.

Choudhury, H., Cary, R., 2001. Barium and Barium Compounds. Concise International Chemical Assessment Document 33. WHO. Available at: www.inchem.org/documents/cicads/.../cicad33.htm.

Cipollini, M.L., Pickering, J.L., 1986. Determination of the phytotoxicity of barium in leach-field disposal of gas well brines. Plant Soil 92, 159. http://dx.doi.org/10.1007/BF02372630.

Coscione, A.R., Berton, R.S., 2009. Barium extraction potential by mustard, sunflower and castor bean. Sci. Agric. (Piracicaba, Braz.) 66, 5. http://dx.doi.org/10.1590/S0103-90162009000100008.

Degryse, F., Smolders, E., Zhang, H., Davison, W., 2009. Predicting availability of mineral elements to plants with the DGT technique: a review of experimental data and interpretation by modelling. Environ. Chem. 6, 198–218. http://dx.doi.org/10.1071/EN09010.

Faraway, J.J., 2002. Practical Regression and Anova Using R. Available at: www.stat.lsa.umich.edu/faraway/book.

Garmo, Ø.A., Røyset, O., Steinnes, E., Flaten, T.P., 2003. Performance study of diffusive gradients in thin films for 55 elements. Anal. Chem. 75, 3573. http://dx.doi.org/10.1021/ac026374n.

Gillman, G.P., Sumpter, E.A., 1986. Modification to the compulsive exchange method for measuring exchange characteristics of soils. Aust. J. Soil Res. 24, 61. DOI: 0004-9573/86/01061$02.00.

He, H., Bleby, T.M., Veneklaas, E.J., Lambers, H., Kuo, J., 2012. Precipitation of calcium, magnesium, strontium and barium in tissues of four Acacia species (Leguminosae: mimosoideae). PLoS One 7, 1–12. http://dx.doi.org/10.1371/journal.pone.0041563.

Heim, M., Hillersøy, M.H., Bleken, M.A., Gautneb, H., Gjengedal, E., 2012. Apatite-biotite-carbonatite (Stjernøy, N-Norway) -potential and obstacles regarding a multinutrient rock-fertilizer. 10th Intern. Congr. Appl. Mineral. (ICAM) 8. http://dx.doi.org/10.1007/978-3-642-27682-8_39.

Heier, K.S., 1962. Trace elements in feldspars - a review. Nor. Geol. Tidsskr. 42, 415–454. Available at: http://foreninger.uio.no/ngf/ngt/pdfs/NGT_42_II_415-454.pdf.

Ivezic, V., Almås, Å.R., Singh, B.R., Loncaric, Z., 2013. Prediction of trace metal concentrations (Cd, Cu, Fe, Mn and Zn) in wheat grain from unpolluted agricultural soils. Acta Agric. Scand. Sect. B-Soil Plant Sci. 63, 360–369. http://dx.doi.org/10.1080/09064710.2013.785586.

Kabata-Pendias, A., 2011. Trace elements in soils and plants, fourth ed. Taylor and Francis Group, ISBN 978-1-4200-9368-1 (Hardback).

Lagas, P., Loch, J.P.G., Bom, C.M., Gerringa, L.J.A., 1984. The behavior of barium in a landfill and the underlying soil. Water Air Soil Pollut. 22, 121. http://dx.doi.org/10.1007/BF00163093.

Lamb, D.T., Matanitobua, V.P., Palanisami, T., Megharaj, M., Naidu, R., 2013. Bioavailability of barium to plants and invertebrates in soils contaminated by barite. Environ. Sci. Technol. 47, 4670. http://dx.doi.org/10.1021/es302053d.

Lee, S.S., Nagy, K.L., Fenter, P., 2007. Distribution of barium and fulvic acid at the mica-solution interface using in-situ X-ray reflectivity. Geochim.Cosmoch. Acta 71, 5763. http://dx.doi.org/10.1016/j.gca.2007.05.031.

Lid, J., Lid, D.T., 1998. Norsk Flora Sixth Edition. Det Norske Samlaget, ISBN 82-521-3754-7.

Lofts, S., Spurgeon, D.J., Svendsen, C., Tipping, E., 2004. Deriving soil critical limits for Cu, Zn, Cd, and Ph: a method based on free ion concentrations. Environ. Sci. Technol. 38, 3623–3631. http://dx.doi.org/10.1021/es030155h.

Madejón, P., 2010. Barium, in: Alloway 2010: Heavy Metals in Soils -Trace Metals and Metalloids in Soils and Their Bioavailability, third ed. Environ. Pollut. Springer 22. http://dx.doi.org/10.1007/978-94-007-4470-7.

Marschner, H., 1993. Chapter 13 nutrient availability in soils. In: Institute of Plant Nutrition, University of Hohenheim (Ed.), Mineral Nutrition of Higher Plants, second ed. Academic Press. Harcourt Brace and Company, Germany, ISBN 978-0-12-473542-2.

Mason, S.D., McLaughlin, M.J., Johnston, C., McNeill, A., 2013. Soil test measures of available P (Colwell, resin and DGT) compared with plant P uptake using isotope dilution. Plant Soil 373, 711–722. http://dx.doi.org/10.1007/s11104-013-1833-7.

Menzie, C.A., Southworth, B., Stephenson, G., Feisthauer, N., 2008. The importance of understanding the chemical form of a metal in the environment: the case of barium sulfate (barite). Hum. Ecol. Risk Assess. 14, 974. http://dx.doi.org/10.1080/10807030802387622.

Myrvang, M.B., Hillersøy, M.H., Heim, M., Bleken, M., Gjengedal, E., 2016a. Uptake of macronutrients, barium, and strontium by vegetation from mineral soils on carbonatite and pyroxenite bedrock at the Lillebukt Alkaline Complex on Stjernøy, Northern Norway. J. Plant Nutr. Soil Sci. http://dx.doi.org/10.1002/jpln.201600328. Scheduled for issue 6/2016.

Myrvang, M.B., Bleken, M.A., Krogstad, T., Heim, M., Gjengedal, E., 2016b. Can liming reduce barium uptake by agricultural plants grown on sandy soil? J. Plant Nutr. Soil Sci. 179, 557–565.

Nolan, A.L., Zhang, H., McLaughlin, M.J., 2005. Prediction of zinc, cadmium, lead, and copper availability to wheat in contaminated soils using chemical speciation, diffusive gradients in thin films, extraction, and isotopic dilution techniques. J. Environ. Qual. 34, 496–507. PMID: 15758102.

Okkenhaug, G., Almås, Å.R., Morin, N., Hale, S.E., Arp, H.P.H., 2015. The presence and leachability of antimony in different wastes and waste handling facilities in Norway. Environ. Sci. Pro. Imp. 17, 1880–1891. http://dx.doi.org/10.1039/C5EM00210A.

Oliviera, W., Carvalho, M.F.B., Almeida, E., Menegario, A.A., Domingos, R.N., Brossi-Garcia, A.L., Filho, V.F.N., Santelli, R.E., 2012. Determination of labile barium in petroleum-produced formation water using paper-based DGT samplers. Talanta 100, 6. http://dx.doi.org/10.1016/j.talana.2012.08.013.

Shaw, C.S.J., Penczak, R.S., 1996. Barium and titanium-rich biotite and phlogopite from the western and eastern Gabbro, Coldwell alkaline complex, northwestern Ontario. Can. Mineral. ISSN: 1499-1276 34, 967. Online.

Smith, E., Hamilton-Taylor, J., Davison, W., Fullwood, N.J., McGrath, M., 2004. The effect of humic substances on barite precipitation-dissolution behaviour in natural and synthetic lake waters. Chem. Geol. 207, 81. http://dx.doi.org/10.1016/j.chemgeo.2004.02.005.

Van Straaten, P., 2006. Farming with rocks and minerals: challenges and opportunities. Anais da Academia Brasileira de Ciências 78 (4), 17.

Zaidonin, H.J., Yap, S.J., 2013. Overcoming multicollinearity in multiple regression using correlation coefficient. AIP Conf. Proc. 4. http://dx.doi.org/10.1063/1.4823947.

Zhang, P.C., Brady, P.V., Arthur, S.E., Zhou, W.Q., Sawyer, D., Hesterberg, D.A., 2001. Adsorption of barium(II) on montmorillonite: an EXAFS study. Colloids Surfaces A Physicochem. Eng. Asp. 190, 239. http://dx.doi.org/10.1016/S0927-7757(01)00592-1.

Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. Environ. Chem. 12, 85–101. http://dx.doi.org/10.1071/EN14105.