Geochemical Characterization of Tea Leaves (*Camellia sinensis*) and Soils for Provenance Studies based on Compositional Data Analysis

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Abstract

Provenance studies on tea (*Camellia sinensis*) are an important tool to reconstruct the origin of tea products. This thesis explores the potential of using solely the ionome (main and trace element concentrations) of tea shoot tips for provenance studies. The emphasis of the thesis is to find element subcompositions which are robust in respect to the various parameters of tea cultivation and production, such as the area, their soils, soil fertilizer and applications of foliar sprays, tea cultivars, plucking/harvesting techniques, manufacturing or leaf grade of the processed tea. For specific discrimination tasks these robust subcompositions can be combined with element subcompositions which are sensitive to one or several tea cultivation and production parameters. The data set consists of ca. 300 leaf and processed tea samples and ca. 130 soil samples. The sampling areas are located in Darjeeling, Assam and Nilgiris in India, in Paraná and São Paulo in Brazil and in Uji and Shizuoka in Japan. All samples, plants and soils, had been treated with four acid digestion methods with HNO_3 , HCl , HClO_4 and HF to achieve a total dissolution. The sample solutions had been analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The element concentrations of the leaf and processed tea samples had been corrected for adhering (soil) particles. Hence, all statistical analysis are based on the corrected concentrations values of Al, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Sr, Ti, Y and Zn. The element concentrations are converted into log-ratios by additive, centered or isometric log-ratio transformations prior to statistical analysis to avoid spurious correlations and to enhance the signal-noise ratio for e.g. the trace elements concentrations. The comparison of the geochemical composition of topsoils, subsoils, mature leaves, shoot tips and processed tea samples is used to establish for each element a qualitative index of robustness with respect to cultivation and production parameters. The elements with a high robustness are considered as very suitable for a provenance analysis without further knowledge about the tea samples. The thesis exemplary shows that with already small element subcompositions a good discrimination by geographical origin is possible if the elements are chosen in terms of their suitability for provenance studies of tea including their sensitivity in respect to specific parameters. The geological source rocks of the tea plantations is one of the major factors for discrimination of tea origin.

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The sampling takes up only few lines in this document but it was - in my eyes - the key to this thesis. I am very thankful to all persons who made my sampling campaigns not simply possible, but an eye-opening, instructive experience.

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1. Introduction

The fascination for provenance analysis on tea comes from the experience that a simple question like "Can we determine the origin of the tea we just bought from the supermarket shelf?" leads to a broad, challenging and interdisciplinary field of research. After compiling this thesis, dedicated only to this question, the answer will still not be an unconditional "Yes, we can!", but rather "We got long strides closer."

Why is it so challenging to determine the geographical origin of tea? First of all, tea is a plant and its interaction with the environment is influenced by soil, climate, slope of the field, neighboring plants, pest attacks, age, cultivar, treatment, etc. Secondly, tea is produced nearly all over Asia, in large parts of Africa and small parts of South America, and also in minor quantities in Australia, North America and Europe. Thirdly, there are many different ways how to manufacture tea, and each type of manufacturing will give its own imprint on the product tea. And last but not least, tea is traded worldwide. It is sorted, blended, sold and resold, until it is finally packed, labeled and put onto the shelf of the supermarket. Considering this complicated, multi-variate setting, it might not even be possible to determine the one tea field in the world where the tea was harvested.

Nevertheless, there is a strong motivation to work on provenance analysis for tea. Tea products cover a wide range of qualities and also a wide range of pricing. Tea is produced under very diverse working and environmental conditions, and, unfortunately, not everywhere the conditions are acceptable. Especially when it comes to human health and human labor no compromises should be made, nor by producers, nor by traders, nor by consumers. Ideally, the price of tea matches approximately the quality, the label on the tea box matches the box' contents and the certificates for environmental and labor conditions conform with the actual local situation. Needless to say, the tea box from the supermarket shelf is not always in accordance with this ideal; and it is not always easy or even possible to point with the finger on who caused the deviation from the ideal. The underlying structures of the tea production and trade which results into the nicely designed tea boxes of small (too small?) prices is too complex to easily pin down one guilty person. Developing a tool to determine the geographical origin of tea will not be

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the solution to guarantee always the ideal of tea production and trading. But if questions are asked about the tea product which can be related to its geographical origin, a provenance tool could help to make the relations between producers, traders and consumers a bit fairer.

It is mandatory to use a multi-variate approach to provenance analysis. No single parameter will ever answer provenance questions in respect to the huge variety of tea products. In this thesis, the analyzed variables cover a broad spectrum of the inorganic elements of the tea leaves. Other parameters, like isotope ratios or organic components, are deliberately excluded: The methods of multi-element analysis are well established, comparably simple and low in cost, and therefore a good deployability for practical purposes is to be expected. Certainly, combining techniques of multi-element analysis with other techniques will increase robustness of the provenance determination, but this would also increase the costs of the provenance tool.

One major obstacle for determining the geographical origin is the blending of tea. Tea is nearly always blended to achieve bigger lots with homogeneous characteristics. These lots can be very small, with sizes of few kilogram, containing only the harvest of one section of one garden, up to sizes of dozens of tons, containing sometimes even leaf material from different continents. The issue of blending is not addressed in this thesis, but discussed in the last chapter 'Conclusions and Outlook'.

Most researchers working on provenance of food items use a reference data set to establish discriminating functions between the groups of their specific data set. In the case of a world-spanning provenance analysis, which should cover all types of tea, this approach would require an enormous reference data set. This project follows an approach which will ultimately help to reduce the necessary sample size for meaningful provenance studies on tea: The elemental composition of tea is caused by parameters of the tea cultivation and the tea production.

The first aim of this thesis is to determine element subcompositions which are influenced by one of the parameters. This opens up two possibilities: a) Previously to the provenance analysis the samples can be grouped by one or more of these parameters by means of their elemental composition. If the sample groups are more homogeneous in terms of e.g. type of manufacturing, type of plucking or type of cultivation, less element variables are needed for robust discrimination functions. b) To establish element subcompositions which are not influenced by critical parameters. These 'robust' element subcompositions are 'first choice' or 'standard' elements to calculate discrimination functions for provenance analysis.

The second aim of this thesis is to demonstrate the possibilities of filtering sample groups and establishing specific element subcomposition for provenance analysis. The prospect of a following project would be to combine various statistical methods with the results of generating element subcompositions and sample subgroups into a holistic model (see also introduction of Chapter 9).

The dissertation is structured by consecutive chapters. Each chapter has a short introduction and a summary of the main findings. The first five chapters give an overview of the tea plant and tea production, the sampled areas, the analytical methods, the data refinement methods and the mathematical tools. Chapter 2 about tea is mainly compiled of published data and occasionally completed by field observations and personal communications from tea garden managers or producers. Chapter 3 describes the sampling areas to provide the basis to interpret the elemental composition of tea in terms of its geographical origin. For this purpose all available geological maps and soil maps had been taken into account for the description of the areas. The section 'Darjeeling' incorporates an own geological mapping, because the published geology of this region was not detailed enough to explain the discriminating parameters for tea samples of Darjeeling. The description of Japan is not included in this thesis, because the data set of Japanese samples consists only of leaf material without the corresponding soils and therefore the Japanese data are not interpreted with respect to their geographical, pedological and geological background. Chapter 4 describes the analytical methods, the data set and the data refinement. All data, which are not represented in the appendix, are provided on the enclosed CD. The sample set from Darjeeling includes 24 sampling spots which had been samples from joint collaboration with the Tea Board. In order to achieve highest possible accuracy and precision for the data, two in-house R-packages had been developed, co-authored by Wiebke Fahlbusch. Both are not further presented within this thesis, but the packages are provided on the enclosed CD. The mathematical tools explained in Chapter 5 are all based on compositional data analysis. The different representations of vector ratios (Section 5.2) are developed within the compass of this thesis to handle element ratios between two samples on a basis of compositional data analysis. In this thesis it is used for element ratios of plant/soil and of young leaf/mature leaf.

The main findings of this thesis are presented in the last five chapters. Chapter 6 evaluates the impact of adhering particles on the elemental composition of tea leaves. All plant data are corrected for adhering particles, and elements with high correction factors are excluded from further analysis. The method of the correction is published in Pos-

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piech et al. (2017) and is included with small adaptations in Section 6.1. The R-package to calculate the correction for adhering particles is published on CRAN (Pospiech and Fahlbusch 2017). Chapter 7 describes the elemental composition of the plant samples and the differences of elemental distribution between the various groups of plant samples. Element subcompositions are determined which are sensitive to the age of the tea leaf, which indicate a contamination through manufacturing, and which have small spread of concentration within one tea garden. Chapter 8 describes the elemental composition of subsoils and the difference to topsoils. This is used to determine element subcompositions which are sensitive to measures of soil management. The second part of the chapter describes which element log-ratios are comparable for soil and leaf samples. In Chapter 9 all findings of the previous three chapters are applied to demonstrate how the various element subcompositions can be deployed for provenance studies. The last chapter gives a summary of the results of this thesis and addresses future tasks.

Throughout the document the publications are cited with the surname of the first author and year of the publication. Initials are only given to disambiguate authors with identical surnames. For Chinese authors the last name in the respective publication is used as author name, in correspondence to the surnames of English author names. All units used in this thesis follow the International System of Units (SI-units). For names of tea gardens the font family 'typewriter' (monospace) is used to disambiguate between geographical names and garden names. For example, 'Tukdah' is a village in Darjeeling District, Tukdah is the tea garden Tukdah Tea Estate, Chamong Tea in Darjeeling District. Generally, all plant data presented after Chapter 6 are corrected for adhering soil particles. The appendix is split into two parts: Selected data tables and all additional figures are provided within this document. The analytical results and further data such as the element selection or limit of detections are provided on the enclosed CD. The 'readme' file contains information about the file types and access.

2. Tea

The word 'tea' has ambiguous meanings because it refers as well as to the plant *Camellia sinensis* (L.) O. Kuntze (*C. sinensis*), to the product and to the beverage. In this thesis the term *C. sinensis* - or simply 'tea' - is used for the tea plant in general. If specification for the species or varieties of the plant is needed, it is referred to as *C. sinensis* var. *sinensis*, *C. sinensis* var. *assamica* or *C. sinensis* 'yabukita' respectively. The term 'processed tea' is used for the agricultural product of the leaves, leaf buds and internodes of the plant *C. sinensis*, prepared and cured by various methods (Gupta et al. 2010).

The chapter describes aspects of *C. sinensis* and processed tea samples (processed teas) which are important with regard to the following chapters: This encompasses the basics about the tea plant and its physiology as well as the main element sources and processes which contribute to the elemental composition of *C. sinensis* and processed teas. Organic compounds of *C. sinensis* are left aside because they are irrelevant for this thesis.

2.1. Tea Plant

2.1.1. *Camellia sinensis*

The tea plant *Camellia sinensis* (L.) O. Kuntze belongs to the genus *Camellia* in the family *Theaceae* and the species *sinensis*. The plant is indigenous to South-East Asia. In China its use for tea brewing is reported for more than 3500 years (Heiss and Heiss 2011). Nowadays the plant is cultivated in many regions of Asia, Africa and partly America (I. A. Ross 2007; Barua 2008). The tea plant grows in a broad range of climatic conditions (Bhagat et al. 2010) but in general *Camellia sinensis* var. *sinensis* (*C. sinensis* var. *sinensis*) grows well under tropical to subtropical climate conditions with high annual rainfall of minimum 1150 mm (Carr 1972) and high humidity (Squire and Callander 2012). The numerous varieties of the plant have slightly different preferences towards their climatic optimum.

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Figure 2.1.: Photo of *C. sinensis* var. *assamica*, left side, and *C. sinensis* var. *sinensis*, right side in Darjeeling. *C. sinensis* var. *assamica* develops 8–14 cm long leaves which are thin and glossy green, while *C. sinensis* var. *sinensis*-plants have smaller leaves (1.6–4 cm long), which are hard, thick and leathery with a matte surface.

The plant is an evergreen small tree which grows in natural environment as high as up to 5 m in height. Occasionally heights up to 9 m are also reported (FOC 14.12.2011). Generally, leaves of *C. sinensis* are light green when emerging from the bud and become dark green as fully grown leaves. Young branches and older roots show a typical purplish red bark while older branches change into a yellowish gray color (Wachira et al. 2013, and references therein). The tea plant is a very heterogeneous outbreeder and most vegetative characteristics of tea show a continuous variation which makes it difficult to differentiate taxa (Banerjee 1992). According to botanical classification there are three main distinct varieties used for tea cultivation, which in some publications are also referred to as own species (Wachira et al. 2013, and references therein). These are *C. sinensis* var. *sinensis*, *Camellia sinensis* var. *assamica* (*C. sinensis* var. *assamica*) and *C. assamica* ssp. *Lasiocalyx* (Cambod race). The numerous types of clones, hybrids and occasionally seed plants are called 'Assam', 'Chinese' or 'Cambod' depending on their morphological proximity to one species (Banerjee 1992). Even for well studied clonal varieties it is sometimes difficult to assign the tea plant exactly to one of the main botanical classified species.

The species *C. sinensis* var. *sinensis* is characterized by small, serrate leaves (1.6–4 cm long), which are hard, thick and leathery with a matte surface (Figure 2.1). The leaf

is directed upwards and is placed at an angle of less than 50° from the stem (Wachira et al. 2013). *C. sinensis* var. *sinensis* prefers the climate characteristic for higher elevations with 500 m NN up to 2000 m NN in subtropical regions and is thus mostly cultivated in hilly regions (Bhagat et al. 2010).

The species *C. sinensis* var. *assamica* is taller and develops long, broad, less serrated leaves (8–14 cm long) which are thin and glossy green. The leaf grows more horizontally with an angle less than 70° from the stem (Wachira et al. 2013). The species prefers higher air temperatures (Tanton 1982) and is therefore mostly cultivated in lowlands and plains such as Assam, NE-India, or Kenya. In this thesis all samples originate from plants which are morphological between *C. sinensis* var. *sinensis* and *C. sinensis* var. *assamica*.

Normally in agriculture the plants of *C. sinensis* are trimmed to approximately waist-high shrubs according to the cultivation techniques. Some farmers in Vietnam are using fully grown trees for tea production (personal communication). Tea plants grown from seeds (seed plants) are generally very robust and can be used for production for about 100 years. Single bushes are reported to be up to 150 years old (personal communication, Ging, Darjeeling). Clonal tea bushes in intensely used tea fields are normally replaced after 40 to 60 years, or as soon as the yield per hectare decreases.

2.1.2. Aspects of Tea Physiology

This section will give a summary of the most important aspects of the tea plant related to this thesis. It is not intended as a comprehensive description of the physiology of the tea plant, especially the often debated topic of detoxification of Al is deliberately excluded.

Roots

The root system and its rhizosphere determines mainly the depth and location of the element source. Microorganisms, e.g. arbuscular mycorrhizal fungi (AMFs), may help the plant to extend its reach considerably beyond the root system (George et al. 1995; Hodge et al. 2001; S. Singh et al. 2008). Typical fungal symbionts of the AMF are *Glomus*, *Gigaspora* and *Acaulospora* (Barua 2008, p.98).

The uptake of elements is confined to the youngest parts of the roots, close to the root apex in the creamy-white, fine feeder-roots. Two third of the feeder roots are located in the upper 30 to 40 cm depth of the soil. The quantity of fibrous roots decreases with depth (Sinha 2010, pp. 100), but feeder roots are also present in 90–100 cm depth (field

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observation in Darjeeling, India, and Araucária, Brazil). Depth and distribution of feeder and mature roots depends largely on local conditions, such as soil properties, rainfall pattern and application of manure or fertilizers (field observations and Marschner 2002; Sinha 2010). If tea plantations are treated with fertilizer applied directly under the bushes the plant develops a shallow and dense fibrous root system down to a depth to 25 cm and a second, less dense fibrous root system located below 40 cm (field observation Brazil, personal communication Masumi Moriuchi, Moriuchi Tea Farm, Shizuoka (Moriuchi)). In Darjeeling District at tea plantations with very steep slopes, manure is applied downhill of the bushes as close to the stem as possible. Through the high erosion rates the manure has less time assimilate with the soil at that specific location. Hence, the fibrous root system of these bushes is more evenly distributed and it is difficult to determine at which depth the quantity of feeder roots notably decreases. As the roots mature, they become woody, shed the root cortex and their epidermis is replaced by a periderm. The periderm has a typically reddish, sometimes red-purple color.

The seminal root or taproot, which exists only for tea plants grown from seeds, is developed as a meter-long, thick, reddish root extending deep into the C-horizon of soils (field observation in Darjeeling). The importance of the seminal root diminishes with plant age, e.g. in Japan it is reported to reach down to only 40–60 cm (Aono et al. 1981). Seed-grown plants develop from the base of the stem with increasing stand age few thick roots which resemble taproots (field observation Darjeeling, India, Sinha 2010, pp. 100). The branches of these roots often penetrate to greater depths than the seminal root (Sinha 2010, pp. 100). Root depth of these roots may extend down to 4–5 m, as reported from Central Africa (Fordham 1972) and from Tanzania (Carr and Carr 1971, pp. 21-47). In flat areas their depth is limited by water-saturated horizons in the soil where the taproot continues growing horizontally above this horizon (field observation in Registro, Brazil, and Assam, India). Root systems located at areas with a water-saturated horizon at rather low depths show a much greater horizontal spread (Sinha 2010, pp. 100). Clonal plants, which don't have a taproot because they are not grown from seeds, develop seven to eight thick adventitious roots growing at an angle from the vertical, which leads to a shallower root system than for seed plants (personal communication of tea planters in Darjeeling, Yamashita et al. 1997).

The root exudation of organic acids, such as oxalic, citric and malic acid, from the tea plant roots is mentioned by many authors based on results obtained by the analysis of root exudates from other plants (Wang et al. 2010; Karak et al. 2015b; Li et al. 2016, and references therein). Morita et al. (2001, 2011) showed that small amounts of citrate

and malate are always secreted while oxalate is secreted to chelate Al^{3+} -ions in the soil solution. Wan et al. (2012) showed in culture experiments that also *C. sinensis* releases protons at its roots during the uptake of cations as a function of the pH of the nutrition solution. It is also reported that the plant's root elongation and growth of tea plant under acidic conditions with high Al^{3+} contents in the soil solution was stimulated rather than suppressed (Konishi et al. 1985; Morita et al. 2001; Tolra et al. 2011). For example Y. M. Chen et al. (2011) showed in hydroponic experiments for *C. sinensis* that Al stimulates the uptake of Ca^{2+} , Mg^{2+} , K^{+} and Mg^{2+} and diminishes the uptake of Fe^{2+} , Cu^{2+} and Zn^{2+} .

Leaves

Figure 2.2.: Sketch of a shoot of *C. sinensis* (source Kumar et al. 1998).

The majority of tea is produced from the apical shoots of the tea plant. Under the point of view of the plant's metabolism this encloses two types of plant organs, the sink and

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source leaves, respectively. Source leaves are leaves which are 'autotrophic' because they are actively performing photosynthesis and produce sugars which are moved to the sink tissues through the phloem part of the vascular system. The source leaves obtain nutrients and water through the xylem part of the vascular system, in which a watery solution containing ions and some organic components moves from the roots to the source leaves, drawn by the evapotranspiration from the leaves (Figure 2.3). Sink leaves, on the other hand, are 'heterotrophic' because they depend for their development on the sugars produced and/or stored in other tissues of the plant.

Figure 2.3.: Schematic figure of the basic elements of the transport systems xylem and phloem (reprinted with permission from Springer Customer Service Centre: Pate (1975)). Principal interchange points between xylem and phloem labeled *I*, regions of loading and unloading of transport channels labeled *L* and *U* respectively, areas specializing in assimilation of raw materials labeled *A*. Directions of flux of solutes are indicated by arrows.

The conversion from sink to source tissue is a developmental transition which results

into a characteristically different chemical composition between autotrophic and heterotrophic leaves (Walworth and Sumner 1987; Turgeon 1989; H. P. Carr et al. 2003)¹.

During the development of the leaf from the apical bud to a fully grown leaf the conversion gradually takes place in many cases when the leaves are expanded by 30–60 % (Turgeon 1989, and references therein). Hence, at the apical shoot of tea plants the bud is purely heterotrophic (sink leaf), the first and second leaf after the bud are mainly heterotrophic with beginning photosynthesis (mainly sink), and the third leaf after the bud is in the middle of the transient stage neither exporting nor importing sugars (Marimuthu et al. 1994; Kumar et al. 1998). The fourth leaf is already nearly fully converted into a source leaf (Marimuthu et al. 1994; Kumar et al. 1998). The timing of the conversion depends on climatic conditions including altitude, on cultivars, on the season, on the time since the last pruning and on the plucking standard (Section 2.3.2), because these parameters determine the rate of the tea shoot development (Smith et al. 1990; Durairaj et al. 2015).

A tea leaf has a life span of approximately two years (Durairaj et al. 2015). The active participation in photosynthesis lasts for six to nine months, depending on cultivar and plantation region (Sinha 2010, pp.102, Durairaj et al. 2015, Kabir and Das 2015, pp. 8–17). The active mature leaf samples (mature leaves) serve in commercially exploited tea bushes as maintenance foliage for the next generation of shoot tip samples (shoot tips).

2.1.3. Tea Ionome

The ionome of a plant is defined as all the mineral nutrients and trace elements found in a plant (Salt 2004; Salt et al. 2008, and references therein) through element uptake or respiration. This includes all metals, metalloids and nonmetals such as N, P, S, Se, Cl and I (Salt 2004). The term ionome was developed to link the plant nutrient signatures with other signatures and profiles, e.g. of genetics, environmental factors, geographic region or farming methods (Parent et al. 2013; Baxter 2015; Huang and Salt 2016, and references therein). In this thesis the term ionome for the elemental composition is used to emphasize the significance of the multi-element approach: thinking beyond individual elements allows the more sensitive detection for elemental variations for discriminating between groups of tea samples (Buccianti et al. 2006; Baxter 2015).

¹ In table I in H. P. Carr et al. (2003) the values for K are displayed in reverse order, showing the higher concentration for the old leaves while in the text of the article it is described that young leaves show higher concentrations of K than old leaves. The latter is correct, because it agrees with findings of other authors.

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The ionome of *C. sinensis* is influenced by the type of cultivar (Y. Chen et al. 2009; Fung et al. 2009; Y. Chen et al. 2010), geographical origin (Marcos et al. 1998; Fernández-Cáceres et al. 2001; Moreda-Piñeiro et al. 2003; Q. Chen et al. 2009), agricultural methods and soil conditions (regulation of soil pH, application of fertilizers, etc.), stand age of the tea plantation (Fung 2003; Fung et al. 2009) and climate, e.g. rainfall patterns. The relative variation of element concentration ranges is small for the nutrients and rather high for trace elements. Despite these differences, there are typical element ranges for tea (Figure 2.4, Szymczycha-Madeja et al. 2012, and references therein).

As a response to the highly acidic soil solution and its toxic Al^{3+} concentration, *C. sinensis* uses a sequestration mechanism by forming Al complexes with organic ligands such as catechins and phenolic acids (Samac and Tesfaye 2003; Morita et al. 2008, 2011, Poschenrieder et al. 2008, and references therein) which leads to the accumulation of Al in the vacuoles of the leaves' epidermal cells (H. P. Carr et al. 2003; Tolra et al. 2011; Matsumoto et al. 1976); Accordingly, *C. sinensis* is considered as an Al-accumulating plant. Some authors have suggested that Al even has a nutritive role in tea physiology (H. P. Carr et al. 2003).

The ionome differs between tissues (Section 2.1.2) and therefore every plant organ has its own characteristic elemental composition (H. P. Carr et al. 2003; Shu et al. 2003; Fung et al. 2009). The description of the ionome is here confined to shoot tips and mature leaves as these plant parts are the relevant ones for this thesis.

Shoot tip

Processed tea is for most tea types produced from shoot tips of *C. sinensis* (Section 2.3.3) and therefore the elemental composition of processed tea is for most elements similar to shoot tips. However, for the elements Al, Cr, Cu, Pb and Zn elevated levels had been reported in processed tea, depending on the production method (Wong et al. 1998; Fung 2003; Ashraf and Mian 2008; Jin et al. 2008; Seenivasan et al. 2008; Salahinejad and Aflaki 2010). Possible sources of contamination are described in Section 2.3.3. Hence, for these elements the ionome of processed teas is potentially altered during production and is not necessarily comparable to the elemental composition of shoot tip.

The main inorganic elements present in shoot tips and processed teas are Al, Ca, K, Mg, P and S (Karak et al. 2015b, and references therein); trace elements with high abundance are Ba, Cu, Fe, Mn, Na, Rb, Sr and Zn, while elements like B, Cd, Co, Cr, Cs, Hg, Li, Ni Pb, rare earth elements (LAs + Y) (REE), Sc, Se, Sn, Ti, V, Y and Zr are usually present at very low concentrations (Figure 2.4, Szymczycha-Madeja et al. 2012,

and references therein, McKenzie et al. 2010). The elements Ag, As, Be, Bi, Cd, Ce, Co, Cs, Ga, Hg, In, Li, Mo, Pb, REE, Sb, Se, Sn, Te, Tl, U, V, Y and Zr are sometimes present at concentrations below the detection limit of analytical methods (Szymczycha-Madeja et al. 2012, and references therein). For these elements exist very few published data.

Shoot tips, consisting mainly of sink tissue, are compared to source tissue relatively enriched in phloem-mobile nutrients, such as K, P and Zn (Schachtman et al. 1998). On the other hand, they are compared to source tissue relatively depleted in elements which are phloem-immobile, like Ca and Al (Figure 2.4).

Mature leaves

As the leaf matures, the ionome changes from the typical sink leaf to the source leaf composition (Wong et al. 1998; H. P. Carr et al. 2003; Shu et al. 2003; Fung et al. 2009). Mature leaf samples have higher levels of Ca, Mg and Mn than shoot tip samples (H. P. Carr et al. 2003; Szymczycha-Madeja et al. 2012, and references therein). Mature leaves progressively accumulate Al (H. P. Carr et al. 2003; Fung et al. 2009; Tolra et al. 2011; Hajiboland et al. 2013); hence the highest Al-concentrations are found in the oldest leaves. Apart from Al there are very few published data for mature leaf samples, e.g. in Figure 2.4 all mature leaf data points originate from H. P. Carr et al. (2003).

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Figure 2.4.: Compilation of published element concentrations of *C. sinensis*. Boxplots are used if there are more than 20 data points per group. For some elements there are data of three mature leaf samples. Number of samples per publication: Ødegård and Lund 1997, N=3, Cao et al. 1998, N=4, Marcos et al. 1998, N=15, Herrador and González 2001, N=48, Matsuura et al. 2001, N=4, H. P. Carr et al. 2003, N=6, Gallaher et al. 2006, N=3, Jin et al. 2008, N=20, Y. Chen et al. 2009, N=8, Salahinejad and Aflaki 2010, N=11, McKenzie et al. 2010, N=135, Hosseinzadegan et al. 2016, N=10

2.2. Tea Soils

The commercial cultivation of tea requires moderately acidic soils with pH optimum between 4 – 4.5 and 5 – 5.5 (Harler 1971; Eden 1976; Ma et al. 2000; Ruan et al. 2007; Paix Mupenzi et al. 2011; Karak et al. 2015b; Pandey 1997; Barua 2008) which have been developed under mesic conditions such as high rainfall and humidity (Fung et al. 2009). Typical soils for tea cultivation are for example in South India laterites or latosols (Ranganatha and Natesan 1985), in China red-yellow podzolic or red-yellow lateritic soils (Fung et al. 2009) or in Kenya soils of volcanic origin (M. K. V. Carr et al. 1987; Othieno et al. 1992).

The acidity of soils in tea gardens is reported to increase with time (Jayman and Sivasubramaniam 1975; Ruan et al. 2004; Zhang and Fang 2007; Li et al. 2016, and references therein), and with the stand age of the plantation (Xue et al. 2006; Han et al. 2007). One reason for the tea soil acidification is obviously excessive application of N-fertilizers containing NH_4^+ , especially in tea gardens located in China (Ruan et al. 2000; Guo et al. 2010; Wang et al. 2010; Cheng et al. 2015; Karak et al. 2015b). Root exudates as a source for acidification are assumed by many authors based on results for other plants (Wang et al. 2010; Karak et al. 2015b; Li et al. 2016, and references therein). Indeed, results of one cultivation experiment had been interpreted that relatively higher pH conditions in tea garden soils, e.g. if the pH increases from 4.0 to 4.5, result into a higher rate of proton release from the tea plant roots (Wan et al. 2012). Other reasons, such as increased organic content through organic manure and litterfall (Fung 2003) or disturbing the soil structure through plowing, may also have a minor impact on acidification (Li et al. 2016).

The very low pH of the tea garden soils has a major impact on bio-availability as well on nutrients as on non-nutrients, which can be toxic at high concentrations, e.g. heavy metals, F or I (Jayman and Sivasubramaniam 1975; Fung et al. 1999; Ma et al. 2000; Ruan et al. 2004, 2006; Han et al. 2007; Zhang and Fang 2007; Y. Chen et al. 2010; Karak et al. 2011; Seenivasan et al. 2016). Because most tea plantations have high stand ages, are situated in regions of leached soils or the geologic source rocks of the region support low pH in the soils, the bio-availability of most elements is comparably high, except for leached elements, for example Ca and Sr. If pH decreases notably below 4 the high concentrations of Al^{3+} and H^+ ions can cause toxicity to the plants and the plant significantly reduces its proton release by the roots (Wan et al. 2012).

Acidification is generally corrected by applying carbonate rocks, such as limestone or

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dolomite, the so-called 'liming'. The frequency and amount of applied carbonate rocks vastly differs between regions and companies. In a garden where carbonate rocks are applied, the frequency ranges between 10 y to 25 y (personal communication of 26 tea garden managers). If recently carbonate containing rock powder had been applied the bio-availability decreases for trace elements and heavy metals, e.g. Al, Fe, REE, Pb, Cd and F.

2.3. Tea Production

In this thesis 'tea production' comprises the treatment of tea bushes like pruning or re-planting, plucking seasons and techniques and tea manufacturing. All steps of the production have an impact on the *C. sinensis*'s ionome. It remains difficult to assign certain element pattern to a specific production step because available data sets are too small-sized or not systematically collected for quantification. This section will give a theoretical overview of which element concentrations of shoot tip and processed tea alter during the steps of tea production with regard to the various production systems included in the present data set.

2.3.1. Fertilizers and Fungicides

Intensive research had been carried out about the tea plant's requirements for nutrients and suitable fertilizers and manure. This section is limited to general effects on the ionome of *C. sinensis* by using fertilizer or manure and possible sources of contamination in analysis of tea soils and leaves.

Commercial production of tea requires intensive fertilizer or compost application in tea fields, usually by several splits per year, especially if the harvest takes place throughout the year (Durairaj et al. 2015; Kabir and Das 2015). Fertilizers can be applied either as foliar spray or as supplement for the soil. Frequency, timing in the year, dose and type of fertilizer varies for each region and between organic and conventional managed tea gardens. Regions with dormancy periods have fertilizer application cycles adjusted to the harvesting periods. However, the frequency and amount fertilizer application is sometimes also used to regulate dormancy periods; For example in some regions the producer can determine the end of the dormancy period by applying fertilizer e.g. four weeks before first plucking round of the harvest period (personal communication Milton Amaya, Amaya Chás, Registro (Amaya), and Masumi Moriuchi, Moriuchi).

The main difference in fertilizing and pest control is obviously found between conventional and organic tea gardens. Because conventional gardens mostly rely on artificial fertilizers with high N, P and K contents, the tea plants are often very well supplied with the major nutrients. On the other hand organic gardens mainly use compost and manure and deficiencies or replacement of nutrients by trace elements with similar chemical characteristics occur more easily.

The regulations about compost composition and production vary considerably between countries and regions. Tea garden compost nearly always contains tea pruning, tea waste, cuttings from weeding and, in the case of India, cow dung. Garden in Darjeeling additionally harvest cuttings of citronella grass or Guatemala grass (*Tripsacum andersonii* J. R. Gray or *Tripsacum laxum* Nash) or other *Tripsacum* species for composting. Some tea gardens enrich the compost with oil cakes as N-source, like castor (Lima et al. 2011, and references therein), coconut, neem, etc., chicken manure, paddy straw, lime or other organic components containing additional N, P, K and S and micro-organisms (personal communication, Kabir and Das (2015)). Accordingly, tracking the input and availability of nutrients and other trace elements in tea soils is for organic tea gardens often impossible.

Foliar sprays are potentially a major source of contamination while sampling tea leaves. Typical foliar fertilizer sprays are ZnSO_4 , MgSO_4 , MnSO_4 and H_3BO_3 (Seenivasan et al. 2008; Durairaj et al. 2015). In organic gardens foliar sprays the Bordeaux mixture, a mixture containing CuSO_4 and $\text{Ca}(\text{OH})_2$, or Copper oxychloride, $\text{Cu}_2(\text{OH})_3\text{Cl}$, is often used as fungicide. Extensive use of the Bordeaux mixture can have a significant impact on Cu concentrations in processed teas (Han et al. 2005).

For most visited tea gardens there are no data collected about the exact timing and frequency of fertilizer application. Whenever possible a general overview of the fertilizers and manure used in the specific tea garden had been recorded. For this thesis, samples had only be taken in sections without very recent treatment (Section 4.1.3) to avoid contamination of the leaves or soil samples by remnants of fertilizers or foliar sprays.

2.3.2. Plucking

The plucking technique determines the ratio between apical buds, mature leaves and leaves in transition in the harvested leaves. As discussed in the sections 2.1.2 and 2.1.3 the ionome differs for nutrients and some trace elements considerably between sink and source tissue and therefore the plucking techniques influence the elemental composition of processed teas.

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The tea plants are usually cut to bushes ('training') with an flat, often horizontal surface, the so called 'plucking table'. Below the plucking table there is a dense layer of mature foliage. From the uppermost centimeters of the plucking table the tea shoots grow from the leaf axils and are harvested in several rounds per season. With each harvest round the plucking table is cut slightly higher to leave a new layer of mature leaves for higher photosynthesis activity (Figure 2.5). Every 2 to 5 years the whole canopy is pruned to remove all younger branches and set up a new plucking table (Squire and Callander 2012).

For each type of processed tea (Section 2.3.3) and for maintenance of the tea bushes there are certain requirements in terms of plucking standard: The most common plucking standard includes the apical bud plus the first two unfolded leaves, called 'two and a bud'. Other plucking standards include plucking only buds - for the highest tea qualities - down to 'hard plucking', where the whole shoot is plucked including mature leaves from the maintenance foliage. The plucking standard has therefore a major impact on the quality of processed tea.

Figure 2.5.: *C. sinensis* var. *assamica*, hand plucked, late in harvest season, Ging, Darjeeling. The actual plucking level can be recognized by the uppermost level of rupture location of shoot remnants. Between the original maintenance leaves (dark green) and the actual plucking table a layer of this season's leaves had been left as maintenance foliage (mature leaves of light green color). From the level of actual maintenance foliage shoot tips in different development stages emerge.

Figure 2.6.: *C. sinensis* 'yabukita', mechanical plucking, begin of harvest season, S. Miguel de Arcaño, Paraná. The plucking table is set by the level of the cutting machine. The shoot tips are mostly in phase and are therefore all approximately at the same stage of development. The plucking standard is set to '2 and bud', but cutting of further developed leaves can not be avoided.

C. sinensis can be plucked either manual, 'hand-plucking', or mechanical, 'machine-plucking', respectively semi-mechanical, e.g. 'shear-plucking'. Hand-plucked tea contains, if pluckers are well trained, only the leaves which should be plucked according to the respective plucking standard. For example, good quality black tea (orthodox black tea) is in Darjeeling produced by 'two and a bud' plucking standard and hence the processed tea contains only buds, the first two leaves and internodes of the shoots (Figures 2.5 and 2.7). For mechanical plucking the growth of shoots developing from axillary buds has to be brought in phase so that the shoots, which are cut at the actual plucking level, match the plucking standard (Figure 2.6). If the shoots are not perfectly in phase, with the occurrence of aperiodic shoots or if the plucking machine is adjusted slightly above or below the actual plucking level, more matured leaves or too young leaves alter the sink-source leaf ratio of the resulting processed tea. Additionally maintenance foliage leaves extend during their development above the actual plucking level and get partly cut during the next round of harvest (Figure 2.8).

Figure 2.7.: *C. sinensis* var. *sinensis*, after hand plucking, late in harvest season, Ging, Darjeeling. The mature leaves of the maintenance foliage are all complete and had been carefully avoided during plucking.

Figure 2.8.: *C. sinensis* 'yabukita', after mechanical plucking, S. Miguel de Arcaño, Paraná. The mature leaves of the maintenance foliage are partly cut and had been accidentally harvested. On the other hand some shoot tips had not been completely harvested.

In the various tea plantation regions different types of machines are used for mechanical plucking. Highest precision in terms of matching a specific plucking standard achieve the fully mechanical plucking methods combined with hormone induced in phase shoot growth as applied in some Japanese companies (personal communication, N. Hashimoto).

2. Tea

Plucking Seasons At Darjeeling the raw material is harvested during four plucking periods in a year: *first flush* (1st flush) is harvested in early spring after the bushes' winter dormancy. During late spring and early summer the *second flush* (2nd flush) is plucked producing a slightly stronger tea. Tea picked in the time between 1st flush and 2nd flush is labeled *in between*. During the raining season the *rains tea* and in October the *autumnal flush* (atm flush) (if the weather allows it) is harvested. High quality teas are manually plucked ensuring that only the freshly grown bud with the first two leaves are collected. The quality of the product tea is also defined by the different grades of tea (Table A.2).

2.3.3. Tea Manufacturing

Each type of processed tea requires its, sometimes specific, plucking standard and plucking season. For example, a 1st flush FTGFOP Darjeeling is plucked manual between March and end of April with the plucking standard strictly '2 and bud', while a stalky OF CTC Assam can be the result of manual or semi-mechanical coarse plucking. In China green tea and oolong of normal leaf grade is produced from '3 and bud' up to '4 and bud' (Wong et al. 1998), whereas high quality leaf grades are made from '1 and a bud' to '2 and bud' (Han et al. 2006).

The tea processing is a multistage procedure to transform the fresh leaves of *C. sinensis* into processed tea ready for brewing. There is a multitude of different ways to process the leaves of *C. sinensis* to processed tea depending on which type, quality and taste of processed tea should be achieved as outcome. Moreover, every company or even every tea factory have their own variations in manufacturing. This chapter focuses only on the general effect of machines used for sencha tea, green tea, black orthodox tea and CTC tea on possible sources of contamination.

Withering For sencha, green tea, orthodox and CTC the plucked leaves are filled into troughs and air is ventilated in order to remove excess moisture from the leaves. If the air is not filtered prior to be pushed through the withering leaves, air borne dust may pollute the plant material (Figure 6.4). Jabeen et al. (2015) describes an increase in Al, Ni and Pb concentration with withering time and explains this increase with pollution from the surrounding area.

Disruption/Rolling The disruption of the wilted leaves destroys the leaves' internal structures at a desired degree to quicken and enhance the oxidation process. For or-

thodox black tea leaves are extensively rolled on steel, gun metal or brass rolling tables (Sinha 2010). In Darjeeling some rolling tables are made of brass with unusual high copper content (personal communication factory managers). The abrasion of the brass rolling tables can reduce the thickness of the rolling tables in the center by millimeter to centimeters per season (personal communication Mr. Pancholi, manager of Marybong Tea Estate, Chamong Tea (Marybong)). For CTC (crush, tear, curl) the leaves are passed, occasionally after a short period of rolling on a table roller, into two stainless steel rollers with a dense mesh of sharp 'teeth'. This procedure cuts and tears the leaves into small parts which ensures a full oxidation in the next step. The rollers of a CTC machinery are especially prone to metal abrasion (Seenivasan et al. 2008). For green tea the disruption of cells is achieved by steaming or pan frying of the leaves. This procedure has no notable source of contamination.

Oxidation/Fermentation For the oxidation process the ruptured leaves are exposed to warm, humid air, either on oxidation benches (black tea) or in several intervals between steaming (green tea). Generally the phase of oxidation/fermentation is of comparable short duration and involves no to very minor invasive machinery. Accordingly no source of contamination is expected by the oxidation step.

Fixation/Rolling/Shaping For some tea varieties the oxidation process is stopped by moderately heating of the leaves, the so called fixation. Between fixation and the drying of the tea the damp tea leaves can then be further processed by rolling, shaping, frying, pressing on bamboo, etc. to achieve a certain shape or special taste. Both procedure steps, fixation and shaping, provide the possibility only for minor metal abrasion but for delicate and/or manual shaping there might be various sources of contamination, depending on local production settings.

Drying Drying removes all remaining moisture of the tea leaves and finishes the tea. Black tea is baked at high temperature by transporting the leaves on a conveyor through a dryer. For green tea each green tea type is dried with a different technique, including dryers similar for black tea production to manual pan frying. In India most orthodox black tea factories use dryers which are heated by wood, coal or sometimes liquefied petroleum gas, which is a possible source of contamination by micro-ash particles or other organic components of the combustion.

2. Tea

Sorting The last step of black tea production is the sorting by particle size, respectively leaf grades (Table A.2), and in CTC additionally by particles density: After drying the tea is loaded into a chained machinery of separators, shakers and sieves of different meshes to separate the various grades of leaves from fiber components and dust grades (Figure 7.9). The sorting line is an additional possible but minor source of metal abrasion. The sorting process may also concentrate non-tea particles in certain leaf grades: For example, fannings or dust grades consists of leaf material separated from all bigger leaf parts by continuously decreasing sieve meshes. The fine particles of machine abrasion are probably found at the leaf grade of similar particle size and which did not got separated by density in a last step, like extensive fanning.

2.4. Summary

The tea plant grows in a broad range of climatic conditions but in general *C. sinensis* var. *sinensis* grows well under tropical to subtropical climate conditions with high annual rainfall and high humidity. The plant is an evergreen small tree which in agriculture fields is trimmed to approximately waist-high shrubs. It is a very heterogeneous outbreeder and most vegetative characteristics of tea show a continuous variation which makes it difficult to differentiate taxa. The numerous types of clones, hybrids and occasionally seed plants are called 'Assam', 'Chinese' or 'Cambod' depending on their morphological proximity to one species.

The root system and its rhizosphere determines mainly the depth and distribution of the element source and depends largely on local conditions, such as soil properties, rainfall pattern and application of manure or fertilizers. The seminal root or taproot is developed as a meter-long, thick, reddish root extending deep into the C-horizon of soils. In flat areas their depth is limited by water-bearing horizons in the soil where the taproot continues growing horizontally above this horizon. Two third of the feeder roots are located in the upper 30 to 40 cm depth of the soil, but feeder roots are also present in 90–100 cm depth. The commercial cultivation of tea requires acidic soils with pH optimum between 4 – 4.5 and 5 – 5.5.

The majority of tea is produced from the apical shoots of the tea plant. Under the point of view of the plant's metabolism, this encloses two types of plant organs, the sink and source leaves, respectively, because the plucking technique determines the ratio of sink to source leaves in the harvested leaves. The apical shoot of tea plants the bud is purely heterotrophic (sink leaf), the first and second leaf after the bud are mainly

heterotrophic with beginning photosynthesis (mainly sink), and the third leaf after the bud is in the middle of the transient stage neither exporting nor importing sugars. The fourth leaf is already nearly fully converted into a source leaf and its active participation in photosynthesis lasts for six to nine months.

The ionome of *C. sinensis* is influenced by the type of cultivar, geographical origin, agricultural methods and soil conditions (regulation of soil pH, application of fertilizers, etc.), stand age of the tea plantation and climate, e.g. rainfall patterns. The relative variation of element concentration ranges is small for the nutrients and rather high for trace elements. The ionome differs between tissues (Section 2.1.2) and therefore every plant organ has its own characteristic elemental composition. Shoot tips, consisting mainly of sink tissue, are relatively enriched compared to source tissue in nutrients which are phloem-mobile, like K, P and Zn. They are relatively depleted compared to source tissue in elements which are phloem-immobile, like Ca and Al. Mature leaf samples have higher levels of Ca, Mg and Mn than shoot tip samples. Mature leaves progressively accumulate Al and the highest Al-concentrations are found in the oldest leaves: As a response to the highly acidic soil solution and its toxic Al^{3+} concentration, *C. sinensis* uses a sequestration mechanism of forming Al complexes which leads to the accumulation of Al in the leaves. Accordingly *C. sinensis* is considered as an Al-accumulating plant and some authors have suggested that Al even has a nutritive role in tea physiology.

Commercial production of tea requires intensive fertilizer or compost application in tea fields, usually by several splits per year, especially if the harvest takes place throughout the year. Fertilizers can be applied either as foliar spray or as supplement for the soil. Compost composition and production vary considerably between countries and regions and accordingly input and availability of nutrients and other trace elements in tea soils is for organic tea gardens difficult to estimate. Foliar sprays are potentially a major source of contamination while sampling tea leaves. Acidification of soils is generally corrected by applying carbonate rocks, such as limestone or dolomite, the so-called 'liming'.

The plucking technique determines the ratio between apical buds, mature leaves and leaves in transition in the harvested leaf material. The ionome differs for nutrients and some trace elements considerably between sink and source tissue and therefore the plucking techniques influence the elemental composition of processed teas. The most common plucking standard for high quality tea products includes the apical bud plus the first two unfolded leaves, called 'two and a bud'.

The tea processing is a multistage procedure to transform the fresh leaves of *C. sinensis* into processed tea ready for brewing. Tea manufacturing includes all or several

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production steps of withering, disruption/rolling, oxidation/fermentation, green fixation/second rolling/ shaping, drying and sorting. The machinery is known to be one source of metal contamination in processed tea through abrasion or chipping. Especially during the step of disruption/rolling some manufacturing methods require very impacting machineries, like the CTC rollers.

3. Characterization of Sampling Areas

Out of the numerous tea growing areas in the world five different areas have been sampled for this study: Darjeeling, Assam and Nilgiris in India, SE-Brazil, and central Japan. These five working areas represent contrasting tea plantation areas which have few parameters of tea cultivation and production in common. This combination of contrasts and common parameter is the key to discriminate between local and general aspects of element uptake by the plants.

The main area is the Darjeeling District of the federal state of West Bengal, NE-India. It is used as a case study for demonstrating the relation between tea ionome and geographical origin. The basis of this case study is a detailed geological map which had been compiled for this thesis from field work and maps and descriptions from other publications.

3.1. India

3.1.1. Darjeeling

The term 'Darjeeling' has ambiguous meanings because it is used as a name for a district, a city, a tea and a tea producing area. In this thesis the district Darjeeling will be always named 'Darjeeling District', the city Darjeeling 'Darjeeling City', the tea Darjeeling 'Darjeeling Tea'. The term 'Darjeeling' is reserved for the tea producing area defined by the areas of the tea gardens which are listed by the Tea Board of India (Tea Board) as *Darjeeling Tea Producers*. The list of these gardens is in the appendix Table A.1.

Geography

The Darjeeling District is the northernmost district of the federal state of West Bengal in the north-eastern part of India. The district covers the foothills of the Himalaya orogen, also called the Lesser Himalaya, enclosed by Nepal in the west, Bhutan in the east and Sikkim in the north. Capital of Darjeeling District is Siliguri, which is situated in the

3. Characterization of Sampling Areas

southern part of the district in the lowland at 120 m a.s.l. The most important hill station is Darjeeling City which is located 45 km north of Siliguri at 2100 m a.s.l. Other important cities are Kurseong (1500 m a.s.l.), halfway between Siliguri and Darjeeling City, Mirik (1600 m a.s.l.) west of Kurseong and Kalimpong (1150 M a.s.l.), 20 km east of Darjeeling City. Between Darjeeling City and Kalimpong the river Teesta cuts a deep, S-N striking valley (ca. 200 m a.s.l.) which divides Darjeeling District into a western and an eastern part.

The climate is influenced by the monsoon causing an alternate wet and dry season (Bhagat et al. 2010). The annual rainfall in Darjeeling varies between 2500 - 5000 mm (Bhagat et al. 2010). The average temperatures are strongly influenced by the altitude.

The southern part of Darjeeling District is characterized by alluvial fans resulting into plains only 120 m a.s.l. These lowland with recent sedimentation controlled by the synorogenic processes consists in very young soils which are relatively coarse grained and rich in pebbles. The main part of the district lies within the Himalayan orogeny and is characterized by steep slopes (20° – 40°) and narrow deep valleys. The heavy rainfalls during monsoon season and huge deforested areas cause serious landslide hazards all over Darjeeling District (Froehlich and Starkel 1993). Due to the frequent landslides and heavy erosion soils are often reworked and seldom show typical soil layering.

Tea is cultivated in the plains of Darjeeling District as well as in the mountainous parts up to 2000 m a.s.l., but only the gardens located in the hilly areas, roughly above 500 m a.s.l., are listed by the Tea Board as *Darjeeling Tea Producers* (Figure 3.1, Table A.1). Tea plantations are covering 30 – 40%, locally up to 80%, while forest cover occupies 38% of the total area (Soja and Starkel 2007). Most of the tea gardens are located in the western part of Darjeeling. As most tea estates are situated in the hilly areas their topography is often dominated by steep slopes with only small areas of relative flatness.

Figure 3.1.: Map of tea estates in Darjeeling District. DEM downloaded from <http://bhuvan-noeda.nrsc.gov.in>, CartoDEM Ver.3, Toposheet No. G45K, tea estates redrawn after Indian Tea Association 1952, projection WGS 84 UTM Zone 45R Pseudo Mercator

3. Characterization of Sampling Areas

Geology

Darjeeling District is located at the southern-eastern part of the Himalayan orogen (Figure 3.2).

Figure 3.2.: Geological map of eastern Himalaya (modified from Acharyya et al. 2017). The red rectangular shows the area of Darjeeling District. The transition between LHS and GHS is drawn as a dashed line because the exact location of the MCT for this region is under debate.

The onset of the formation of the Himalayan orogen started approximately 48 Ma ago with the collision of the Indian and the Eurasian Plate. During the orogeny the geological units now building the Himalayas got thrust and imbricated mainly parallel to the continental margin in northern direction. This resulted into an approximately 2400 km long arc of the Himalayas range with all four domains being present the whole lateral extension.

Himalayas is generally divided into four geologic domains (Heim and Gansser 1939; Gansser 1964; Le Fort 1975; Yin 2006). These are from south to north: (1) the sub-Himalaya Sequence (sub-HS) of Cenozoic age, (2) the LHS, Palaeoproterozoic meta-sedimentary rocks which are non-fossiliferous low-grade metamorphic, (3) the GHS, Neoproterozoic and early Paleozoic gneisses and aplitic granites, and (4) the Tethyan Himalaya Sequence (THS), a marine, fossiliferous sequence.

Structurally, there are four major thrusts systems between the geologic domains. These are from south to north: The (1) Main Frontal Thrust (MFT) as the thrust placing the Neogene Siwalik of the sub-HS above the Quaternary deposits of the Alluvium (e.g. Gansser 1964; Yeats and Lillie 1991; K. A. Singh et al. 2001; Yin 2006); the (2)

Main Boundary Thrust (MBT), defined by Heim and Gansser (1939) as the fault placing the LHS above the sub-HS; the (3) MCT, very roughly defined as a fault and thrust zone between the LHS and GHS (Heim and Gansser 1939; Gansser 1964; Le Fort 1975; Searle et al. 2008); and the (4) South Tibet Detachment (STD) juxtaposing the THS over the GHS (Burg and Chen 1984; Burchfiel et al. 1992; Ding et al. 2001; Yin 2006).

The definition and exact location of the MCT is subject of an ongoing debate (Ghosh 1956; Acharyya and Ray 1977; Lal et al. 1981; Ray 2000; Catlos et al. 2004; Dasgupta et al. 2004; Harris et al. 2004; Searle and Szulc 2005; Searle et al. 2008; Anczkiewicz et al. 2014; Mottram et al. 2014a). In the eastern Himalaya between the Daling group of the LHS in the footwall and high grade gneisses of the GHS in the hanging wall there is a zone of an inverted Barrovian sequence (Lal et al. 1981; Acharyya 1989; Dasgupta et al. 2004; Harris et al. 2004; Mottram et al. 2014a; Chakraborty et al. 2016), from some authors also referred to as 'zone of inverted metamorphism': The grade of metamorphism increases from the topographically lower areas with increasing altitude. This zone of inverted metamorphism has in the Darjeeling-Sikkim area a thickness of about 2000 m (Goscombe et al. 2006 and field observations). Based on field observation and the definition of Dasgupta et al. (2004), Goscombe et al. (2006) and Gupta et al. (2010) here, this zone will be addressed as the Main Central Thrust Zone (MCTZ) (Figure 3.3). This zone is either interpreted as being a sequence or partly a sequence in the hanging wall of the LHS, or that parts of the sequence are within the GHS implying that the MCT is located also within this zone (e.g. Goscombe et al. 2006).

Due to high weathering rates and the steep topography with frequently occurring landslides and heavy erosion rocks on the surface are often displaced. Huge blocks gradually sliding down the hills can be easily mistaken for outcrops and lead to misinterpretation of orientation of bedding and/or foliation as well as location of formations. Poor road conditions and dense forest areas or tea plantations makes it difficult to find reliable outcrops.

The geological map of Darjeeling compiled for this thesis is mainly based on field observations of 2011, 2012 and 2015 with the help of a compilation of petrology described by Mottram et al. (2014b) and Bhattacharyya and Mitra (2014) and maps from Mohan et al. (1989), citing Roy (1976) and Lal et al. (1981), Mukul (2000), citing Schwan (1980), and Goscombe et al. (2006). For field observation outcrops of recent road works, small streams and fresh landslides had been chosen if the total setting of the location indicated that the rocks are still originally placed. The map is shown in Figure 3.14.

3. Characterization of Sampling Areas

Figure 3.3.: Geological map of Darjeeling-Sikkim Himalaya (modified from Grujic et al. 2011 which is a map compiled of Schelling (1992), Goscombe and Hand (2000), Goscombe et al. (2006), Bhattacharyya and Mitra (2009), Kali et al. (2010), and Kellett et al. (2010)). The transition between the LHS and the GHS is marked as MCTZ interpreting the inverted Barrovian sequence as an ~2000 m thick shear and thrust zone.

In Darjeeling District there are three to four geological units:

1. **Quaternary:** The valley of the river Teesta and the plains of the Darjeeling District are covered by alluvium and debris originating from the Himalaya hinterland as a result of the ongoing Himalayan orogeny.
2. **Daling Group (LHS):** In the topographically lower areas the Daling unit of the LHS is cropping out
3. **Main Central Thrust Zone:** The part of Darjeeling District which is situated in the the Himalayan orogenic belt is dominated by the sheared and thrust package of amphibolite facies metapelite schists and gneisses of the MCTZ.
4. **Kangchenjunga Gneiss (GHS) ?:** Whether or not in the topographically highest peaks the Kangchenjunga Gneiss (GHS) (Kangchenjunga Gneiss) as a unit of the GHS is cropping out remains under debate.

Quaternary The Quaternary sediments of Darjeeling Districts are built by the proximal parts of the Teesta Mega Fan, lobe 1A and 3 (Chakraborty and Ghosh 2010), and the fans of the rivers (from east to west) Mahananda, Balason and Mechi. These alluvial sediments formed during the last 2.0 Ma in response to the thrusting of the Siwalik of the sub-HS along the MFT above the foreland sediments MFT (Powers et al. 1998; Wesnousky et al. 1999). Close to the mountain front there are coarse gravely piedmont sediments, along the rivers there are channel fills of gravel, sand and clay and related to the megafans there are pebbly, coarse to fine sand and mud sediments (Chakraborty and Ghosh 2010). The setting in Darjeeling District is generally dominated by sheet-braided sandy stream deposits (Tunbridge 1981; Chakraborty and Ghosh 2010, and field observations).

Figure 3.4.: Outcrop of Daling Group (LHS). See meter-sized stick on the right rim for scale.
N 27°06'16, E 88°14'30, WGS 84

Figure 3.5.: Detail of outcrop from Figure 3.4. The greenschist grade phyllites have often a crenulated cleavage.
N 27°06'16, E 88°14'30, WGS 84

Daling Group (LHS) The Daling Group (LHS) (Daling Group) is mainly composed of low grade metamorphic rocks such as greenish phyllite, massive quartzite, and (not exposed in Darjeeling District) greywacke and epidiorite (Acharyya et al. 2017 and references therein). In Darjeeling District it crops out as greenish colored, fine-grained mica-schist, interbedded with up to 15 cm thick quartzite layers. In some locations the rocks seem to be of relatively higher metamorphic grade which was determined by the occurrence of small garnets in the schist layers.

The Daling Group had been mapped in the north of Darjeeling District in the adjacent valley of the river Rammam north of Shree Dwarika Tea Estate, Chamong Tea (Shree Dwarika), in the west in the lower sections of Teesta Valley Exports Limited (Teesta

3. Characterization of Sampling Areas

Valley) and in the south in the lower section of Makaibari Tea Estates (Makaibari).

Main Central Thrust Zone The MCTZ is the major unit in Darjeeling District and nearly all tea estates are located on its gneissic rocks. The metamorphic grade of this zone of inverted metamorphism gradually changes from greenschist facies in the structural lowest levels up to amphibolite facies with abundant kyanite in the structural highest levels (Goswami 2005; Goscombe et al. 2006; Dasgupta et al. 2009; Mottram et al. 2014a,b; Gaidies et al. 2015 and field observations). For this study this sequence had been subdivided into three metamorphic zones by isogrades of indicator minerals. These are from the structural lowest levels of the MCTZ to the higher levels a) the garnet-muscovite zone (Grt-Mu-zone), b) the staurolite zone (St-zone) and c) the kyanite zone (Ky-zone).

Figure 3.6.: Outcrop of metasandstone of garnet-muscovite zone with preserved sedimentary layering. See tapeline on left margin for scale.

N 26°54'38, E 88°13'04, WGS 84

Figure 3.7.: Outcrop of schist of garnet-muscovite zone.

N 27°06'10, E 88°14'43, WGS 84

The structurally lowest Grt-Mu-zone consists of low- to middle-grade fine to medium grained garnet-staurolite schist intercalated with metasilstones and occasionally metasandstones. The original sedimentary layering is well preserved in metasilstones and metasandstones (Figure 3.6), while metapelitic layers show a well developed schistosity defined by aligned mica and chlorite minerals (Figure 3.7). The schistosity is planar towards the footwall of the Grt-Mu-zone and changes to more crenulated cleavage in structurally higher parts. In layers of undulated micaceous cleavage occur deformed quartz lenses and fine to middle grained garnets (Mottram et al. 2014b). The thickness of the layers reaches from several millimeter up to meter scale.

The mineral content varies strongly depending on the original sedimentary rocks. The

main minerals are: quartz $\pm$ biotite $\pm$ muscovite $\pm$ garnet $\pm$ staurolite $\pm$ chlorite $\pm$ feldspar and accessories. In a example sample of Mottram et al. (2014b) located on the ridge between Gielle Tea Estate (Gielle) and Namring Tea Estate (Namring) (Location N 27°00'21, E 88°10'22, WGS 84) the mineral composition is 50 % Mu, 30 % Qu, 10 % Bi, 3 % Grt, 2.5 % Chl and 1.7% St. In an example sample of Bhattacharyya and Mitra (2014) located in Sivitar Tea Estate, Ambootia Tea Group (Sivitar) (Location N 26°52'45, E 88°20'05, WGS 84) the mineral composition is 47 % Qz, 20 % Fsp, 20 % Bi, 8 % Grt and 5 % Mu.

The garnet minerals have a grain size of 1 mm up to maximum 3 mm. The staurolite occurs as fine, max. 0.8 cm long needles oriented along the foliation (Figure A.2).

Figure 3.8.: Outcrop of staurolith zone along the street between Tumsong and Lingia. N 27°01'59, E 88°11'10, WGS 84

Figure 3.9.: Hand specimen from outcrop in Tumsong. The macrostructure of the rock shows small scale folding. The gneiss includes small, ubiquitous garnet grains, visible by brownish weathered remnants. N 27°02'16, E 88°10'30, WGS 84

The St-zone begins with the occurrence of middle grained staurolite minerals, i.e. when the $\{001\}$ plane of staurolite grains is visible with the eye. The zone consists of medium to coarse grained garnet-staurolite(-kyanite) gneisses with very distinct foliation (Figure 3.8). The gneisses consist of crenulated mica-rich foliation bands consisting mainly of biotite. These micaceous foliated bands with a well defined foliation are intercalated with quartzitic layers (Figure A.4). There are frequently elongated deformed porphyroclasts of quartzo-feldspathic material. In some localities the main foliation is superimposed by a second schistosity resulting into a crenulated cleavage in foliated bands with high mica content (Figure A.3) or, in layers of higher content in quartzite and feldspar, folding of the original layering (Figure 3.9).

3. Characterization of Sampling Areas

The main minerals are: quartz $\pm$ garnet $\pm$ feldspar $\pm$ staurolite $\pm$ biotite $\pm$ muscovite $\pm$ kyanite and accessories. In an example sample of Mottram et al. (2014b) located on the south side of Tukdah Tea Estate, Chamong Tea (Tukdah) (Location N 27°01'58, E 88°20'30, WGS 84) the mineral composition 40 % Qz, 20 % Plg, 19 % Mu, 10 % Bi, 5 % Grt, 5 % St and 1% Ky. Quartz and feldspar grains show a shape preferred orientation within the foliation. Garnets are ubiquitous and isomorph developed with grain sizes up to 1 cm. Generally the abundance of muscovite is notably decreased compared to the Grt-Mu-zone and the gneisses of the St-zone have a darker aspect. The staurolite and the higher content in biotite is probably a result of the breakdown of light micas and chloritoids (Deer et al. 1992). In more iron-rich layers of the schist this would be

and in more magnesium-rich layers of the schist this would be

Figure 3.10.: Outcrop of kyanite zone along a street. Block is probably slightly displaced which results into a rotated foliation compared to original setting.
N 26°58'35, E 88°09'02, WGS 84

Figure 3.11.: Boulder of kyanite zone in a stream 3.5 km distance to uppermost point of the ridge. The reddish colors result from iron-oxides and weathered garnets. In the upper part of the boulder kyanites can be seen by bright blueish colors).
N 26°58'56, E 88°08'34, WGS 84

The Ky-zone starts with the occurrence of kyanite minerals with grain sizes up to 1 cm. The zone consists of fine to coarse grained kyanite-biotite-staurolite gneisses which are partly folded (Figure A.5). In most outcrops the gneisses show a strong foliation defined by the general orientation of the quartz ribbons of cm-scale to dm-scale in a dark biotite(-staurolite) matrix (Figure 3.10 and Figure 3.11). Dark, biotite-rich layers are alternating with gray layers of fine-grained quartzo-feldspathic material, porphyroblasts of kyanite

and rare porphyroclasts of feldspars. In leucosomes or more felsic layers the kyanite, quartz and feldspar content is significantly higher. The main minerals are: biotite $\pm$ kyanite $\pm$ garnet $\pm$ quartz $\pm$ feldspar $\pm$ staurolite $\pm$ sillimanite and accessories. In an example sample of Mottram et al. (2014b) located on the ridge 5 km east of the border city Mane Bhanjang (Location N 27°00'45, E 88°22'50, WGS 84) the mineral proportions are 40 % Qz, 17 % Plg, 17% K-Fsp, 17% Bi, 3.5 % Grt, 3% Ky and 0.5% Sil. Like in the St-zone garnet grains are ubiquitous with varying grain size distribution, but may reach up to 5 cm grain size in m-scale quartz lenses. Muscovite is (nearly) not present in the gneisses, probably to further breakdown due to higher metamorphic peak conditions.

Kangchenjunga Gneiss In the topographically highest areas of Darjeeling District, in Darjeeling City and around Tiger Hill, outcrops show amphibolite grade gneisses. They are very poorly exposed and often highly weathered. The gneisses are characterized by elongated (cm - m scale), undulating and deformed felsic lenses of varying composition embedded in grayish to dark-grayish, melanocratic matrix. The coarse grained gneiss appears (locally) as Augengneiss. There are meter-sized quartzite lenses with garnets up to 6 cm (Figure 3.13).

Some researchers describe this amphibolite grade gneisses as a klippe of the Kangchenjunga Gneiss of the GHS. This could presumably only be confirmed by dating the gneisses which has not been accomplished yet.

Figure 3.12.: Outcrop of amphibolite gneiss in Darjeeling city.
N 27°00'53, E 88°15'07, WGS 84

Figure 3.13.: Outcrop of amphibolite gneiss in Darjeeling city. On the left lower corner of the foto the hole is caused by weathered garnet (for unweathered garnet see Figure A.8). See leaf for scale.
N 27°01'34, E 88°15'45, WGS 84

3. Characterization of Sampling Areas

Structure The foliation of the Barrovian sequence in Darjeeling is slightly dipping to NE (Gupta et al. 2010 and field observation). Bhattacharyya and Mitra (2014) describes the leading edge of the thrust between MCTZ and Daling Group as a ~2 m thick NNE–dipping greenschist facies phyllonite zone with the foliation dipping 35° towards 037° (Location N 26°52'45, E 88°20'05, WGS 84). This is about parallel to the observed foliation for the whole region. The contact between MCTZ and Daling Group is in most locations associated with a topographic break.

In the northwestern part of Darjeeling District the valley stretching between the village Mane Bhanjang and the village Jorethang is defined by a major strike-slip fault zone: In Tumsong the gneisses facing the valley exhibit a nearly vertical dipping foliation striking parallel to the valley NE–SW.

Figure 3.14.: Map of geological units in Darjeeling District. DEM downloaded from <http://bhuvan-noeda.nrsc.gov.in>, CartoDEM Ver.3, Toposheet No. G45K, projection WGS 84 UTM Zone 45R Pseudo Mercator

3. Characterization of Sampling Areas

Soils

The soils of Darjeeling hill areas are mainly sandy-silty regoliths showing notable variations, depending on elevation, degree of slope and geological source material (Soja and Starkel 2007; Gouvernement of West Bengal 2012 and field observations). They do usually not exceed 1–2 m thickness and are very permeable with high infiltration rates (Froehlich and Starkel 1993). Generally the soils have very low pH values and are predominantly reddish till brownish in color: Reddish color can mainly be found in soils with greenschist facies gneisses or sandstone as source rock. Typical soils developed of the greenschist facies gneisses are found for example north of Darjeeling in Shree Dwarika, or north of Mirik, in Nagri Farm Tea Estate, Chamong (Nagri Farm) and Dhajea Tea Estate, Chamong Tea (Dhajea), or in the south of the district, in Castleton Tea Estates, Goodrike (Castleton) and Makaibari: They are deep red to orange red and have locally a very high content in light micas. Brownish colors developed at amphibolite facies gneisses, schist or shale or/and with high organic content in soils, like in forests (Gouvernement of West Bengal 2012; Kundu et al. 2012 and field observations). Soil developed of amphibolite facies gneisses are found for example in western part of Darjeeling District, in topsoil sample (topsoil), Marybong or Chamong Tea Estate, Chamong Tea (Chamong), or in the southern part of the district, in Margeret's Hope Tea Estate, Goodrike (Margeret's Hope), Singell Estate (Singell) or Castleton. Also the grain size of soil components is regulated by the source rock: Units with high content of quartzite and sandstones produce very coarse grained, skeletal soils. Units of mica schists or garnet schists like the Daling series, soils become sandy with high content in coarse particles. On the the low-grade metasediments like the Siwaliks soils become silty and clay rich (Figure 3.15).

Figure 3.15.: Map of soils in Darjeeling District. Map of tea estates in Darjeeling District. DEM downloaded from <http://bhuvan-noeda.nrsc.gov.in>, CartoDEM Ver.3, Toposheet No. G45K. Soil map redrawn after Seghal (1991) (Selvaradjou et al. 2005). Projection WGS 84 UTM Zone 45R Pseudo Mercator

3. Characterization of Sampling Areas

3.1.2. Assam

The term 'Assam' has ambiguous meanings because it is used as a name for the federal state in India, a type of tea plant, a tea and a tea producing area. In this thesis the federal state of India will be named 'Assam State', the tea plant '*C. sinensis* var. *assamica*', the tea Assam 'Assam Tea'. The term 'Assam' is reserved for the tea producing area which covers the broad plains of the Brahmaputra river in Assam State.

Geography

Assam is a federal state of Republic of India situated in the north-eastern part of the country with an area of approximately 79 000 km². The state covers the valley of Brahmaputra river in the north and the Barak river in the south. The Brahmaputra valley is defined by the eastern Himalaya in the north, the Mishmi Hills in the north-east, the Nagar-Patkai range in the south-east and the Shillong plateau with the Mikir Hills in the south. The capital of Assam State is the city Dispur which lies within the city region of Guwahati in central Assam State. Along the river Brahmaputra there are the cities Tezpur, 130 km east of Guwahati, Jorhat, 160 km east of Tezpur, Dibrugarh, 120 km north-east of Jorhat, and Tinsukia, 50 km east of Dibrugarh. At the border between Assam State and the federal State Arunachal Pradesh lies the city Namsai, which is located 65 km north-east-north of Tinsukia. Tea is produced mainly in the Cachar region in the southern part of Assam State and along the valley of the Brahmaputra river in the northern part. Because all samples originate from the region around Tinsukia and Namsai the following description will focus on this tea producing area in Upper Assam (Figure 3.16).

In the Brahmaputra valley the annual precipitation varies from 2100 to 2900 mm (Bhagat et al. 2010). During the summer months the precipitation pattern is characterized by the south-west monsoon while the winter is the dry season. The heavy precipitation during monsoon causes surplus water and the regularly occurrence of floods. During the dry season occasionally the tea producing areas suffer water deficit due to very low precipitation (Bhagat et al. 2010).

Geology

The Upper Assam Basin is structurally a basin between two convergent margins (Raju and Mathur 1995). It is enclosed in the north by the eastern Himalayas through the MFT, in the east by the Mishmi Hills through a thrust and in the south by Patkai Hills through

the Naga thrust (Lahiri and Sinha 2012 and references therein). The interpretation of seismic data acquired by the oil companies reveals that the basin is disturbed by several NE–SW trending faults. The upper layers of the basin fillings are alluvial sediments from the mountain-fed river system of the Brahmaputra river (Sinha and Friend 1994). The sources of the alluvial material is mainly the tectonically active Himalaya (Singh 2006) and consequently the parent rocks of the alluvium include igneous, metamorphic and sedimentary rocks. The mineralogy of the alluvium is dominated by resistant minerals, like quartz and the comparably higher amount of zircons, while easier weathering minerals like mica, feldspar and chlorites are notably decreased, especially in older parts of the alluvium due to the high rate of surface weathering (Chakravarty et al. 1979)

Soils

Soils in Assam are mainly alluvium-derived soils which are moderately developed with occasionally minor content of clay in weak argillic horizons (Baruah et al. 1983; Chakraborty et al. 1984; Chakravarty et al. 1985; Pal et al. 2001). They are generally acidic and rich in organic carbon with the concentration of the nutrients being fairly high in the upper soil layers (J. Singh et al. 1995). The dominant clay mineral is illite with chlorite and/or kaolinite as a minor phases (Chakraborty et al. 1984).

In Upper Assam Karak et al. (2015a) carried out a study about soils in tea estates with a total of 991 samples from 15 tea estates (Figure A.9): The authors classified the soils as Oxisols (Histic Haplaquox) according to the USDA classification. The pH values, measured with a soil:water ratio of 1:2.5, range in median between 4 and 5, with a minimum at 3.6 and a maximum at 6.8. Soils with a pH higher than 5.6 are probably less acidic due to water-logging or application of lime. Litterfall and regular pruning of tea bushes and shade trees in combination with weak decomposition leads to relatively high contents of Total Organic C (TOC) in most analyzed tea estates (Karak et al. 2015a).

In the visited tea estates (Maud/Sewpur Tea Estate, Chamong Tea (Maud), Sankar Tea Estate, Division Gohain, Chamong Tea (Gohain), Platzhalter (Platzhalter)) the grain size distribution of the soils is sandy to silty and well drained. Additionally meter-deep drainage trenches in the tea gardens help to prevent water-logging. On a km-scale the soils are very homogeneous. But there is a strong variability in grain size within m-scale due to old channels and benches of former tributaries of Brahmaputra river (Figure 3.18) while the regularly occurring floods erode and re-sediment material in the topsoil layer.

Figure 3.16.: Map of tea estates in Assam State and Arunachal Pradesh. DEM downloaded from <http://bhuvan-noeda.nrsc.gov.in>, CartoDEM Ver.3, Toposheets No. G46E and G46F. Tea estate locations and river redrawn after satellite image 2018 (Google satellite), projection WGS 84 UTM Zone 46R Pseudo Mercator

Figure 3.17.: Soil profile in Gohain.

Figure 3.18.: Tea plantation in Gohain. Tea bushes, which are still in winter dormancy are without young shoots and appear as dark green, while flushing tea bushes are light green colored. The time offset of the 1st flush is caused by grain size variability of soils which leads to different water availability for tea bushes.

3. Characterization of Sampling Areas

3.1.3. Nilgiris

The term 'Nilgiris' has ambiguous meanings because it is used as a name the Nilgiris District in the federal state Tamil Nadu in South India and a tea producing area. In this thesis the term 'Nilgiris' is reserved for the tea producing area which covers the southern area of the Nilgiri Hills.

Geography

The Nilgiris district is the westernmost district of the federal state Tamil Nadu in the South India. The neighboring federal states are Karnataka to the North and Kerala to the West. The main cities are Udagamandalam (Ooty) in the central part, Coonoor in the southern part, Kotagiri lying 10 km South-West of Coonoor and Gudalur 25 km North-East of Ooty. The district is situated within the Nilgiri Massif which is located at the juncture of the Eastern and Western Ghats mountain ranges (Samuel et al. 2014). North of the the Nilgiri Massif lies the Mysore plateau, and towards the North-West its bounded to the continuation of the Western Ghats by high scarps (Rajakumar et al. 2007; Valdiya and Sanwal 2017). In the South-West and the South-East the Nilgiri mountains rise abruptly from the surrounding plains from approximately 300 m a.s.l. to plateaus of hilly ranges and broad valleys between 1000 m and 2000 m a.s.l. (Valdiya and Sanwal 2017). The prominent peaks rise up to 2500 m to 2600 m (Seshagiri et al. 1982).

The climate of the district is dominated by the South West Monsoon and the North East Monsoon. The total annual rainfall ranges between 5000–2500 mm in the western regions, 2000–1500 mm in the eastern and southern regions and in average 1200–900 mm (Caner et al. 2007). Due to the elevation the temperatures are moderate with a mean minimum of 5 °C in winter and 24 °C in spring and summer (Caner et al. 2007).

Geology

The Nilgiris Massif is an Archaean granitoid–gneissic crustal domain of the extensive South Indian granulite terrain (M. M. Raith et al. 1999, and references therein). It is bounded in the north by the Moyar shear zone and in the south by the Bhavani shear zone (M. M. Raith et al. 1999; Samuel et al. 2014, and references therein). The Nilgiris Massif is predominantly constituted of hypersthene-bearing, medium-coarse grained enderbite to charnockitic rocks (M. Raith et al. 1988; C. Srikantappa et al. 1988). The charnockites are of intermediate, tonalitic to granodioritic, composition (Rajesh and Santosh 2004, and references therein). The enderbites are described as garnetiferous and

non-garnetiferous layered gneisses (M. Raith et al. 1988; Rajesh and Santosh 2004, and references therein). The garnetiferous intermediate charnockite exhibit calc-alkine characteristics and are geochemically close to the tholeiitic series (Rajesh and Santosh 2004). The Nilgiris Massif is dissected by frequently occurring, ENE-WSW trending pyroxene-bearing doleritic dykes. There are rare metasedimentary intercalations of amphibolite facies, including quartzites and gneisses, and granulitic xenoliths of mafic composition (C. Srikantappa et al. 1986; M. M. Raith et al. 1999; Rajesh and Santosh 2004).

The sampled tea gardens are all located within the area which is predominantly composed of charnockites. At the eastern slopes of the Nilgiri Massif two outcrops are describes by Samuel et al. (2014): Close to Kil Kotagiri Tea Estates (Kil Kotagiri), about 1 km north of the garden, the outcrop consists of mafic granulite of clinopyroxene + garnet + plagioclase + amphibole. About 5.5 km of north of Havukal Tea Estate (Havukal) and 6 km north of Kil Kotagiri a charnockitic outcrop is described to contain quartz + plagioclase + kalifeldspar + orthopyroxene + garnet $\pm$ biotite. In the central part close to the garden Highfield Tea Estate (Highfield) charnockite of the same composition is cropping out. About 7 km north of Coonoor the composition of the charnokites are described to be slightly different with quartz + plagioclase + kalifeldspar + garnet + biotite $\pm$ orthopyroxene. They are intercalated with the mafic granulites.

Soils

Road cuts and boreholes reveal that the weathering profile of soils in the Nilgiris ranges from less than a meter to 20 m, with a maximum of 32 m (Seshagiri et al. 1982; Jaiswal et al. 2011) The sub-tropical climate with its intense weathering altered the gneissic source rocks into lateritic clays, clayey loams and loams (Natarajan et al. 1997). The weathered zone between the clayey soils and the source rock is approximately one meter thick (Parthasarathy and Vaidyanathn 1974). Some areas reveal also patches of red sandy soils (Parthasarathy and Vaidyanathn 1974).

The tea plantations are mainly based on sandy loam to sandy clay loam which are very deep and well drained (Natarajan et al. 1997). The topsoils reach down to 0.3–1 m and the subsoils have a thickness between 3–4 m (Natarajan et al. 1997, and personal communication). They are characterized by very low pH around 4 (personal communication) and have generally a poor nutrient status. In the eastern parts the tea soils are classified as Inceptisols according to the USDA classification, and in the western parts as Ultisols (Natarajan et al. 1997).

3.2. Brazil

3.2.1. São Paulo

Geography

São Paulo is a federal state in the east central part of Brazil with its south-eastern border being the coast line. North and north-west of São Paulo lie the federal states Minas Gerais and Rio de Janeiro, north-east the federal state Mato Grosso do Sul and south-east neighboring lies the federal state Paraná. The state capital and the largest municipality is São Paulo City, located in the south eastern part close to the coast. Tea is cultivated in two communities ca. 180 km south of São Paulo City, i) south of the city Registro and ii) close the village São Miguel de Arcanjo.

Registro is situated in the Vale do Ribeira, 30 km west of the coast. The average elevation is 25 - 30 m a.s.l. and the morphology is characterized by the alluvial plains with dense ramification of the river Ribeira. The tea fields are planted on slightly elevated terraces of clay-sandy sediments, locally enriched with gravels (J. L. S. Ross n.d.). Being close to the coast with very low topographical gradient the area is regularly affected by floods. The climate, subtropical and with generally high humidity, is influenced by Registro's location between coast and the coastal range to its north-west.

São Miguel de Arcanjo is situated 150 km west of coast and inside the coastal range (Cinturão Orogênico do Atlântico) at 700 - 900 m a.s.l. The neighboring cities are Registro, 70 km south, Capão Bonito, 40 km south-west, Pilar do Sul, 30 km north-east and Itapetininga, 30 km north. The climate is subtropical with average temperatures between 22°C and 14°C. Although the tea fields are situated in a mountainous setting slopes are moderate. In some fields meter-sized boulders are very frequent.

Geology

The city Registro is located in the Ribeira Tectonic Depression area (J. L. S. Ross n.d.). North of Registro this depression is limited by an ENE-WSW elongated block of gneissic, biotite rich monzogranite, the Gnaiss Itapeúna of the Atuba unit (Perrotta et al. 2005). South and southeast of this granitic block the Ribeira Tectonic Depression is filled with fluvial Cenozoic sediments (Embrapa Solos 2013; Souza Lima et al. 2016). The sampled tea fields are located on a terrace of sandy to loamy and fanglomeratic sediments of the Pariquera-Açu Formation (Melo 1990; Perrotta et al. 2005, Figure A.10). These fanglomeratic sediments have a low ZTR (zircon-turmaline-rutile) index (Hubert

1962), indicating that these are rather immature sediments which formed in alluvial fans (Moraes et al. 1991).

Figure 3.19.: Geological section of Ribeira Depression, source: Melo (1990, Figure 7). 1 - Quaternary sediments 2 & 3 - rubbles of terraces 4 - Pariquera-Açu Formation, fanglomeratic sediments 5 - Pariquera-Açu Formation, fluvial sediments 6 - Siete Barras Formation 7 - Precambrian basement

In the village São Miguel de Arcanjo the base rocks of the two tea fields are constituted of two very distinct geologies. The main field, the division 'Matriz', is located very close to the northern limit of the Apiaí terrane of the western part of the Ribeira Fold Belt (Campanha and Sadowski 1999). It is located inside a small occurrence of the São Miguel Arcanjo Granite (Perrotta et al. 2005), a post-tectonic granite of the Neoproterozoic orogenies (Janasi et al. 2001). The outcrop consists of a slightly foliated porphyritic to porphyroid, hornblende-biotite, K-feldspar-rich monzogranite (Leite et al. 2007). The second tea field, the division 'Filia' approximately 10 km WNW of 'Matriz', is located in the Phanerozoic Paraná Sedimentary Basin (Perrotta et al. 2005).

Soils

The soils around Registro are mainly organosols in and along the recent and ancient river channels, and cambisols in the rest. The sediment terrace, on which the sampled tea fields are located, is covered by latosols (Oliveira et al. 1999). The soils are red-yellow to deep red colored, intensely weathered, silty to sandy with minor contents of clay consisting mainly of quartz grains and kaolinite. The latosols in this area are described to have a very low capacity to retain cations and need frequent fertilizer application to be usable for agriculture (Oliveira et al. 1999; Oliveira 2014).

At São Miguel de Arcanjo the soils of the tea gardens are also intensely weathered, dystrophic, brownish-red latosols (Oliveira et al. 1999). They are silty to clayey with a varying sand component and minor amount of small pebbles. Source rocks are of

3. Characterization of Sampling Areas

igneous (granitic) and metamorphic origin and they are former forest soils (Oliveira et al. 1999). The top soils (ca. 20 cm) are rich in organic matter and are regularly treated with compost of saw mill waste and chicken feces (3:2).

3.2.2. Paraná

Geography

Paraná is a federal state south eastern part of Brazil, its southern border being the coast line of the Atlantic Ocean. North of Paraná lies the federal state São Paulo, north-west Mato Grosso do Sul and south Santa Catarina. West of Paraná lie neighboring the states Argentine Republic and the Republic of Paraguay. The state capital and the largest municipality is Curitiba, located in the eastern part close to the coast. Tea is cultivated close to the community Araucária, ca. 30 km south-west of the city Curitiba.

The tea fields of Paraná are located 13 km south-west of the community Araucária. The altitude is around 930 m a.s.l, at the southern rim of the Curitiba Basin. The plateau is gently undulating due to a dense drainage system of sediment filled stream beds.

Geology

The area is part of the Curitiba Tectonic Domain. In the community Auracária crop out the units of the Atuba Complex and Cenozoic deposits (Sato et al. 2003). The Atuba Complex is characterized as a tonalite–trondhjemite–granodiorite (TTG) suite (Faleiros et al. 2011). It consists of mainly mylonitic, migmatic orthogneisses which alternate with tonalitic-trondhjemitic to granodioritic leucosomes and plagioclase-rich, mesocratic neosomes (Sato et al. 2003; Faleiros et al. 2011). There are frequently occurring amphibolitic lenses. The mylonitic, migmatic gneisses are composed of hornblende, microcline, plagioclase, quartz and biotite. The mesocratic neosomes contain additionally hypersthene and/or diopside and garnet (Sato et al. 2003) with titanite as very frequent accessory mineral (Sato et al. 2003; Faleiros et al. 2011).

In the area of the sampling locations the gneisses are joined by the schists of the Atuba Complex (Figure A.10): They are often rich in biotite, partly migmatic, and intercalated with quartzites and arkoses. The cenozoic deposits are mostly alluvial sediments of sandy to coarse-sandy grain size.

Soils

The tea garden in Araucária is mostly situated on latosols, and only on the alluvial sediments are argisols (Embrapa and Emater 2006).

The latosols are deeply weathered (up to 2 m), yellowish to reddish soils, with generally low fertility and low pH. They are porous and well drained and poor in rocky components (Santos et al. 2008; Embrapa Solos 2013). The argisols are characterized by a accumulation of clayey components in the B horizon while the A horizon may contain high percentages of sandy components. This leads in combination with low organic content to a reduced capacity to retain nutrients.

4. Description of Samples and Methods

The section 'Samples' gives an overview of sampling and various sample groups, which will be used as grouping parameter for statistical discrimination techniques. The section 'Methods and Analysis' describes all steps of data acquisition from the original sample material to the raw data output of the instruments. The section 'Data Handling' gives details about how the raw data are processed and selected for the final geochemical data set which is used for the provenance analysis.

4.1. Samples

Samples have been collected between 2011 and 2016. In total there are 438 analyzed samples of which 96 samples are also used in Pospiech (2012).

4.1.1. Types and Groups of Samples

The sample set consists of two types of samples, plant tissue and soil. For most soil samples there are leaf samples of one or two bushes growing exactly above the soil sampling location, but not for each leaf sample exists a corresponding soil sample. In total there are 81 sampling locations with corresponding leaf and soil samples.

Plant Samples

The sample type 'plant' splits into two groups: Processed tea sample (processed tea) refers the ready made product 'tea', which are processed and dried leaves, and plucked leaf sample (plucked leaf) refers to the leaf samples plucked from the tea bushes. The latter group is divided into two subgroups: The shoot tip sample (shoot tip) refer to the young shoots of tea bushes and mature leaf sample (mature leaf) refer to leaves which are fully matured.

The plucked leaf sample 'shoot tip' consists of the first two to three leaves of a shoot, leaf buds and internodes of the shoot (Figure 2.2). These are the parts of *C. sinensis*,

4. Description of Samples and Methods

Table 4.1.: Overview of number of analyzed samples in respect of type, group and subgroups.

Type	Group	Subgroup	Number of samples
Plant	plucked leaf	shoot tip	160
		mature leaf	27
			187
	processed tea	green	26
		black	85
		gunpowder	1
		oolong	2
			114
			301
	Soil	topsoil	41
		subsoil	96
			137

which are harvested for tea production according to plucking standards 'two and a bud' and 'three and a bud' (Section 2.3.2). Depending on the climate conditions and the cultivar of *C. sinensis* the second and third leaf of the shoots could already have undergone the transition from sink to source leaf (Section 2.1.2). This implies that the sample subgroup shoot tip is a mixed sample of sink and source leaves with unknown mixing ratio under the point of view of plant physiology. It can be assumed that the percentage of sink leaves is higher than that of source leaves, especially in shoot tip samples plucked 'two and a bud'.

The sample subgroup 'mature leaf' consist of leaves which are at least two months old and at maximum four years. The latter are plucked leaves which consist only of source leaves. Mature leaves are generally not plucked for tea production, but during machine plucking (Figure 2.6), semi-mechanical/ shear plucking and rough hand plucking parts of mature leaves come into the mass of harvested shoot tips.

For the sample group of processed tea it has to be distinguished between *single garden processed tea* and *blend*. The single garden processed teas have been either collected directly from the tea garden's factories, covering most of the visited gardens, or had been provided by head offices of the tea producers or official tasting samples for tea traders. Blends can be either I) samples originating from trusted sources like head offices from tea producers or II) unconfirmed sources like packaged teas from supermarkets.

Soil Samples

The sample type 'soil' splits into two subgroups: Topsoil refers to the upper layers of soil while subsoil sample (subsoil) refers to the soil sampling volume underneath the topsoil. The transition between topsoil and subsoil is approximately where the influence of the soil management ceases, indicated e.g. by changing of the soil color.

Due to very different soil characteristics of the four sample regions the transition zone between topsoil and subsoil varies: In Darjeeling, having generally shallow soil coverage due to very steep slopes, topsoil reaches down to approximately 15 cm and subsoil is sampled from 15 cm to approximately 30 cm depth. In the alluvial sediments of Assam the depth of transition between topsoil and subsoil varies strongly between the locations, but generally topsoil reaches down to approximately 25 cm and subsoil is sampled from 25 cm up to 45 cm depth. In the strongly weathered soils of Brazil the transition between topsoil and subsoil is approximately at 15 - 20 cm depth.

4.1.2. Origin of Samples

Plucked leaf samples originate from seven regions: Darjeeling, Nilgiris and Assam in India, São Paulo and Paraná in Brazil and Uji and Shizuoka in Japan. Soil samples originate only from four regions: Darjeeling and Assam in India and São Paulo and Paraná in Brazil. Processed tea samples originate from six of the seven regions of plucked leaf samples, only of Paraná in Brazil there are no processed tea samples, because production had not yet started during sampling. Additionally there are processed tea samples of several regions of Nepal ($N = 12$), China ($N = 1$), Sri Lanka ($N = 1$), Iran ($N = 1$) and Uganda ($N = 1$).

The samples are not equally distributed in terms of their origin (Table 4.2). The majority of samples originates from Darjeeling, while from the other six regions the number of samples is comparatively small. Results of regions with less than six samples are considered as tentative studies.

Darjeeling had been sampled four times: in May 2011, April 2012, April and May 2014 and October 2015. Assam had been sampled twice, in late March 2012 and November 2015. All other regions had been sampled only once: São Paulo and Paraná during September 2013, Nilgiris during late October 2015 and Shizuoka and Uji during June 2016.

4. Description of Samples and Methods

Table 4.2.: Overview of number of analyzed samples in respect of type, country and region.

Type	Country	Region	Number of samples
Plant	India	Assam	26
		Darjeeling	167
		Nilgiris	25
			218
	Brazil	Paraná	5
		São Paulo	37
			42
	Japan		1
		Shizuoka	10
		Uji	13
			24
	Nepal		7
		Dhankuta	5
			12
	Others		5
			301
Soil	India	Assam	13
		Darjeeling	90
			103
	Brazil	Paraná	12
		São Paulo	22
			34
			137

4.1.3. Sampling

Sampling took place during different seasons of the year, spanning all three high quality shoot seasons 1st flush, 2nd flush and atm flush (Section 2.3.2). The majority of the samples had been collected during the flushing seasons of the respective tea producing area.

All plucked leaf and soil samples originate from tea gardens. Tea gardens are organized in sections implying that the area of one section is treated exactly the same and that the field and factory management is very similar throughout the garden. Only few processed tea samples from Nilgiris might include leaf material from fields of so called

'small growers' (Tea Board India 2017), which have their own and undocumented field management.

Sampling locations were chosen due to following considerations:

- at least 30 m distance to streets and field paths
- at least 100 m distance to busy streets
- minimum distance to other sampling location should be more than 50 m
- location should be "inside" a section to avoid effects of the field margin, like more exposure of the bushes, other competitive plants, etc.
- avoiding direct proximity of small streams, villages, compost sites, etc.
- even bush density, avoiding patchy sections
- representativity of the section of the garden
- sections without recent fertilizer application (Section 2.3.1)

For the sampling of the soils first step was to spade a hole of 30 - 45 cm depth, and describe layering, gradation, grain size, skeleton and quantity of roots of the fresh soil exposure. In Brazil a tool equivalent to the Pürckhauer driller was used for sampling. Then topsoil sample was drawn from homogenized soil material of the upper 15 - 20 cm and subsoil sample was drawn from the homogenized soil material from 15 - 20 cm down to 30 - 45 cm depth. The soil samples were stored in fresh and labeled bags of stable plastic and as soon as possible dried at 105°C. Each soil sample contains more than 100 g dry mass.

Plucked leaves had been sampled with clean and dry hands imitating hand plucking for tea production. Seed plant bushes had been sampled separately, while for clonal bushes shoot tips and mature leaves are plucked from several adjacent bushes. Shoot tips and mature leaves were kept in separate clean, unused and labeled paper bags. Plucked leaf samples had been air dried during field campaign and as soon as possible oven dried at 105°C. Each plucked leaf sample contained at least 12 g dry mass.

Processed tea samples had been partly derived from head offices or official retailers of the respective companies, but mostly directly from the tea garden's factories. Processed teas from factories are either from before sorting ('drier mouth'), after sorting, or after reblending. Reblended samples are in most cases blends of the day's production and only in few cases blends of several days' production. Reblended samples are very comparable to processed tea samples from the head offices.

4.2. Sample Preparation and Analysis

4.2.1. Sample Preparation and Digestion

The aim of the sample preparation is to obtain a residual free, clear sample solution. The reproducibility of the element measurements is better for completely digested samples because the concentrations are independent of the interaction time between sample and the acids as compared to partial digestion procedures (Ruppert 1991; Dean 2014). According to Hoenig (1995), Matsuura et al. (2001), and Welna et al. (2013, and references therein) the following protocol is highly suitable for the tea plant samples. 32 samples are dissolved together as series of which at least one sample is a blind sample (blind) and one to three samples are international reference materials. The blinds are included to ensure that the handling was clean and without remarkable contamination during the digestion process.

The plant samples were dried unwashed at 105 °C and grounded to < 60 µm grain size in an agate ball mill in order to avoid contamination through metals. For the digestion process 400 - 500 mg of the homogenized powder of plant material were used.

The soil samples were dried and split into three parts. For pH measurement one part were sieved to < 2 mm in grain size. The pH was measured in 25 mL 0.01 mol/L CaCl₂ solution according to DIN 19684 Part 1 with 10 g of the soil. For geochemical analysis one part were dried at 105 °C and then grounded in an agate ball mill to < 60 µm grain size. Out of the homogenized powder 100 - 120 mg of soil were used for the digestion process. The aliquots of plant and soil samples were fully digested with a mixture of ultra-pure concentrated HNO₃, HClO₄ and HF in closed ultra clean PTFE vessels (PicoTrace Göttingen). Detailed description is enclosed in the appendix (B.1).

4.2.2. Analysis

The clear solutions (soils and plants) were analyzed in batches of 90–150 samples, including the blinds of the digestion series and the international reference materials samples. Analysis were done by ICP-OES and ICP-MS of about 50 elements. For several elements there are more than one analysis, because the measurement routines on ICP-MS and ICP-OES include several masses (ICP-MS) and spectral lines (ICP-OES). Because the routines do not always include exactly the same masses or spectral lines samples may have different number of analysis for each element. For example, for Barium there are for some samples in total eight analysis, the masses Ba 135 and Ba 137

of the ICP-MS and the spectral lines Ba 233.527 (axial and radial), Ba 455.403 (axial and radial) and Ba 493.408 (axial and radial) of the ICP-OES. Out of these one to eight element data for each sample one data point per element is selected as analytical result (Section 4.3.1). The selection is listed in Table B.6 in the appendix.

The calibration solutions for the ICP-MS and ICP-OES are given in the appendix (Table B.5). For the ICP-MS analysis (machine *Elan DRC II*, *Perkin Elmer*) the same calibration solution was used for all samples (Table B.2). For the ICP-OES analysis for the sample types soil and plant two different calibration solutions had been used in order to adjust the characteristics of the calibration solution to the type of sample solution. Both types of ICP-OES calibration solutions had been slightly changed according to adjustments to general elemental composition of plant samples and varying detection ranges of the machines *Optima 3300 DV* (*Perkin Elmer*) (Table B.3, until May 2015) and the machine *5100 VDV* (*Agilent*) (Table B.4, from June 2015 onwards).

For ICP-MS analysis all samples had been spiked with an Internal Standard (IS) (Table B.1). Accordingly the elements Be, Ge, Rh, In and Re are not included in the results.

4.2.3. Limit of Detection, Precision and Accuracy

The limit of detection (LOD) is calculated on basis of the blinds of each batch of samples. Each batch of samples includes between 3 to 12 blinds. Because blinds are samples the resulting LOD takes into account the handling of the samples and not only the LOD of the machines.

$$LOD = 3 * stdev(blind_1, blind_2, \dots, blind_n) \quad (4.1)$$

Only results above the LOD had been accepted.

Precision and accuracy are ensured by using the international plant reference materials GBW 10052, BCR-129, NCS DC 73349, NJV 94-5 as well as the in-house standard TW-45. Each analysis of a reference sample includes the process of digestion and analysis via ICP-MS and ICP-OES. The referenced values of the 27 analyzed reference samples are given in the appendix (Table B.10).

For each reference sample precision and accuracy had been calculated to assess the quality of analytics for each series and each sample batches analyzed by ICP-MS and ICP-OES. Accuracy is the relative proximity of the measured value from the reference

4. Description of Samples and Methods

value in percent and is calculated by

$$Accuracy[\%] = \frac{|Conc_{measured} - Conc_{reference}|}{Conc_{reference}} * 100 \quad (4.2)$$

Precision is calculated the relative deviation from the median of all measured values of the respective reference sample ($Conc_{median}$):

$$Precision[\%] = \frac{|Conc_{measured} - Conc_{median}|}{Conc_{median}} * 100 \quad (4.3)$$

The precision is calculated by the relative deviation, instead of using the range or the standard deviation, because the total data set of analyzed reference material samples contains between 3 to max. 45 analyses per each type of reference material (Gorard 2005). The calculation of the precision is based on a compiled data set of 104 analysis from several similar projects. Hence the precision is based on 5 analysis for BCR-129, 5 for NJV 94-5, 49 for NCS DC 73349, 24 for GBW 10052 and 21 for TW-45.

The LOD, accuracy and precision of each analysis batch are the basis to select for each element the best analysis for the respective sample type out of the rawdata of ICP-MS (different masses) and the rawdata of ICP-OES (different spectral lines). The accuracy and precision of the selected element analysis of each reference sampled are given in the appendix (Table B.15 and B.19). Average accuracy and precision for the elements was better than 5% for all main elements and better than 10% for most trace elements (Table 4.3). For plants the elements Cr, Co, Mo, Sn and ultra-trace elements like e.g. the heavy REE show an average precision between 10% - 20%.

Table 4.3.: Averaged accuracy and precision of the international reference plant and rock standards used for this thesis. All values are given in %. Averages (mean) are calculated for plants by BCR-129 (N=2), GBW 10052 (N=11), NCS DC 73349 (N=3), NJV 94-5 (N=3) and for soils by TW-45 (N=5), TW-59 (N=2) and JLK-1 (N=1).

	Plant Acc.	Plant Prec.	Soil Acc.	Soil Prec.
Al	5.8	3.7	1.1	0.7
As	20.6	15.4	13.4	19.8
Ba	4.0	2.4	2.6	2.2
Ca	11.7	2.3	3.1	1.6
Cd	21.6	6.6	26.4	24.9
Ce	10.4	12.3	6.9	5.6
Co	14.1	6.7	6.3	2.9
Cr	36.1	29.2	35.3	28.2
Cs	9.1	10.7	7.8	20.7
Cu	8.1	5.2	6.3	2.3
Dy	11.5	10.0	8.3	21.7
Er	7.9	9.3	10.1	21.8
Eu	26.4	27.6	8.9	20.5
Fe	13.6	10.4	1.8	2.6
Gd	13.1	12.2	6.1	23.3
Hf	44.0	23.6	18.9	22.9
Ho	9.9	11.3	8.6	21.6
K	12.5	11.4	3.5	2.5
La	10.4	11.6	14.8	8.9
Li	8.5	9.8	7.3	8.1
Lu	11.8	12.2	7.3	16.8
Mg	9.8	2.3	3.2	2.2
Mn	13.7	8.1	2.8	1.8
Mo	26.6	21.1	21.4	24.7
Na	8.9	7.4	2.7	1.7
Nb	98.0	19.4	11.0	2.6
Nd	8.0	9.3	8.7	21.3
Ni	10.1	7.4	3.1	1.8
P	12.5	9.6	3.4	1.0
Pb	13.4	9.4	5.7	16.2
Pr	11.0	11.0	9.4	21.1
Rb	12.9	12.6	11.8	21.6
S	12.1	9.0	11.1	2.5
Sb	14.8	13.2	15.2	22.9
Sc	18.4	98.8	6.3	3.7
Sm	9.9	10.8	9.7	20.8
Sn	45.2	35.7	16.6	18.9
Sr	7.1	4.2	2.7	3.0
Ta		42.2	45.2	23.3
Tb	10.2	10.8	9.5	20.5
Th	21.0	19.8	32.3	22.5
Ti	35.4	10.6	1.8	1.5
Tl	17.5	8.3	16.0	25.9
Tm	10.8	10.0	13.3	22.7
U	28.9	19.9	29.5	9.4
V	158.9	29.8	2.5	2.2
Y	29.5	11.2	11.6	21.0
Yb	20.4	10.8	24.9	20.4
Zn	4.9	3.3	3.0	3.1
Zr		27.6	20.8	8.1

4.3. Data Handling

The aim of the data processing is to make the final concentration data independent of the sample groups, sample lots, type of machines and analytical protocols: A sample of processed tea, sampled in 2013 and analyzed in 2014, should be comparable to a shoot tip, sampled in 2015 and analyzed in 2016.

Data processing includes all steps of data treatment from the raw data export from the machine until the final concentrations used in the statistical analysis. These steps are:

1. Calculation of element concentrations for the sample solutions from the raw data of ICP-MS and ICP-OES. For ICP-MS the IS (Table B.1) is used for calculating the concentration.
2. Drift-correction
3. Subtraction of the values of the blinds from all other samples in order to remove background values.
4. Corrected concentration of the sample solution ($\mu\text{g/L}$) are converted into dry weight (d.w.) concentration (mg/kg).
5. Selection of one datum for each element and each sample based on accuracy and precision of adjacent reference samples and range between LOD and sample concentration (Section 4.3.1).
6. Check for outliers and irregularities
7. In case of plant samples: Correction for adhering particles (Section 6)

4.3.1. Selection of Element Data

As mentioned in Section 4.2.2 for each sample and for each element there are several data points which have to be reduced to one datum as result. The selection of data points depends on a) the matrix of sample solution, e.g. plant or soils, b) the concentration range, c) the comparability between calibration solution and sample matrix, d) the LOD of the respective spectral lines of ICP-OES or masses of ICP-MS and e) the measurement itself, e.g. if there had been enhanced oxidation rate in the ICP-MS for certain elements or minor plasma instabilities at the ICP-OES for certain elements on that specific day of analysis. Hence, there is no general selection for each type sample matrix but the selection is calculated for each digestion series and sample type based and accuracy

and precision of the measurement. The accuracy and precision is determined for each reference sample for all elemental data points (Section 4.2.3) and weighted by 1:3, e.g. if the ICP-OES spectral line Ba 455.403 for the reference sample XY had an accuracy of 5 % and a precision of 3 % the ratio is 3.5 %. The spectral line or the mass with the smallest ratio is selected as the best data point for this element in this reference sample, e.g. if Ba 455.403 (axial) of ICP-OES has a ratio of 3.5 % and Ba 135 of ICP-MS has a ratio of 4.1 % the Ba 455.403 is chosen.

For each element and each sample type there is a preferred data point. For example, out of the eight Ba data points Ba 455.403 (axial) is the preferred line for choosing the Ba concentration. The preferred data point is determined for each sample type by the best accuracy:precision ratio over all analyzed reference samples for the respective sample type. In order to use for one sample type as often as possible the same line or mass for one element there is a flexibility of 5 % in the ratio in favor to the preferred data point: If the best accuracy:precision ratio is not the preferred data point and less than 5 % smaller than the preferred data point then the preferred data point is selected, e.g. if Ba 455.403 has a ratio of 6 % and Ba 135 of 4 % then still Ba 455.403 is selected if it is the preferred data point for the respective sample type.

The selection of data points is calculated per digestion series because series of samples (Section 4.2.1) are combined to different sample batches for ICP-MS and ICP-OES analyses (Section 4.2.2). The combination of series is often different for ICP-MS and for ICP-OES analyses. If there is more than one international reference sample included in the series the accuracy:precision ratios are averaged for the data points. The selection of data points calculated for the reference samples is applied on all non-reference samples of the same series. The selection was calculated by the in-house R-packages Pospiech and Fahlbusch (2018) and Pospiech (2017) and is listed in the electronic Appendix.

The prerequisite of this selection technique is a very good comparability of reference material and sample material within one series. Consequently for this thesis all series of plant material include at least one sample of GBW 10052 and all series of soil material include at least one sample of TW-45.

4.3.2. Software ¹

Maps had been produced by QGIS (QGIS Development Team 2018). All data processing and plotting had been carried out within the free statistical software R Core Team (2017). The R packages used for data handling are 'ICPData' (Pospiech and Fahlbusch

¹The package 'ratios' is published on CRAN (Pospiech and Fahlbusch 2017)

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2018), 'ICPSubfunctions' (Pospiech 2017), 'data.table' (Dowle and Srinivasan 2017), 'dplyr' (Wickham et al. 2017), 'tidyr' (Wickham and Henry 2018), 'gnumeric' (Antal 2017), for representation 'ggplot2' (Wickham 2009) and 'xtable' (Dahl 2016) and for calculations are 'compositions' (Boogaart and Tolosana-Delgado 2008), 'MASS' (Venables and Ripley 2002), 'ratios' (Pospiech and Fahlbusch 2017). The calculations done by the package 'ratios' are described in the sections 5.2 and 6.1.

5. Mathematical Tools

The results of this thesis are derived mainly of concentration data. Concentrations are values which represent parts of the whole, e.g. parts per million (ppm) or weight percent (wt%), and contain only relative information. Following the notation introduced by Aitchison (1986) the elemental composition of samples is represented by a D -dimensional, positive vector, the concentration of each element being one of the D vector components. Vectors are written in bold font, $\mathbf{x}$, which are denoted by $\mathbf{x} = [x_1, x_2, \dots, x_D] = [x_i]_{i=1, \dots, D}$. Such vectors are subject to several constraints and therefore do not belong to the space of D -tuples of real numbers, R^D , but to the D -part simplex (S^D): the set of vectors of positive components and constant sum. Hence, before using statistical tools and algorithms developed for numbers of $\mathbb{R}$ the vectors have to be moved from the S^D into the $\mathbb{R}$ by logarithmic ratio (log-ratio) transformations. In this thesis various log-ratio transformations are used and all results of concentration values will be presented as log-ratios. Another reason to use log-ratios is to enhance the signal-noise ratio for trace elements: Ratios help avoiding artefacts through analytical errors, e.g. machine error or weighing inaccuracy¹. The logarithm allows to compare very different concentration levels, e.g. wt% with ppb. As a rule calculations are based on the natural logarithm ($\ln$), only for certain figures the decimal logarithm ($\log$) was used for ease of understanding.

5.1. Compositional Data and Log-ratio Transformations

Properties and characteristics of numbers in the S^D , called *compositions*, were first time fully described by Aitchison (1982, 1986). Elemental concentrations are one type of compositional data with the characteristic that they are so called "closed" compositional data: Each element concentration is a component of a D -part composition, all parts of the composition are constrained to a constant sum and in this thesis all components are considered as strictly positive. For example, if concentrations are given in wt%, they

¹tea powder is highly hydrophile and gaining up to 5 wt% within 30 min of exposure to air, unpublished data

5. Mathematical Tools

have values between 0 and 100 and the sum of all components will be 100. Accordingly, this type of compositional data provide only relative information.

If compositional data are closed the components of a vector are algebraically linked with each other, e.g. if one part increases from 10% to 20% at least one other part has to diminish in order to keep the constant sum. Hence, if concentration data are used without taking the linkage of parts into account spurious correlations and biases in the results may occur (Filzmoser and Hron 2008). Furthermore, it is necessary that results are consistent between an analysis with all components of a composition and an analysis of a subcomposition (selection of components). This 'subcompositional coherence' is one important requirement which has to be fulfilled for all analysis. For example the relation between the elements Na, Ca and K should be identical for all possible subcompositions, e.g. if the analysis was carried out with all elements of a sample, or the subcomposition Na, Ca, K, P, S or the subcomposition Na, Ca, K. For detailed description of compositional data please refer to e.g. Aitchison (1986, 2003), Buccianti et al. (2006), Pawlowsky-Glahn and Egozcue (2006), Pawlowsky-Glahn and Buccianti (2011), and Pawlowsky-Glahn et al. (2015).

There are several possible log-ratio transformations. Here only a small overview of the basic equations is given for the transformations which are used in this thesis. For a detailed description of properties, advantages and disadvantages of the various log-ratio transformations please refer to Egozcue and Pawlowsky-Glahn (2011).

The simplest log-ratio is between two parts, x_i and x_j , of a composition:

$$\text{pwlr}(\mathbf{x}) = \left[\ln \left(\frac{x_i}{x_j} \right) \right]_{i,j=1,2,\dots,D} \quad (5.1)$$

The calculation of pairwise logarithmic ratios (pairwise log-ratios) of a data set can be understood as producing for each sample a matrix which contains log-ratios of each element against each element. If a data set consists of n samples with y elements the result of a pairwise log-ratio transformation are n matrices of $y \times y$ entries.

If this simple log-ratio is applied for a fixed denominator x_D it is called additive log-ratio (alr) (Aitchison 1986):

$$\text{alr}(\mathbf{x}) = \left[\ln \left(\frac{x_i}{x_D} \right) \right]_{i=1,\dots,D-1} \quad (5.2)$$

The alr of $\mathbf{x}$ has one component less than $\mathbf{x}$ and each part is algebraically independent.

Using a centered log-ratio (clr) transformation (Aitchison 1986) all parts of the compo-

5.1. Compositional Data and Log-ratio Transformations

sition are set into relation to the geometric mean (g_m) of the composition:

$$\text{clr}(\mathbf{x}) = \left[\ln \left(\frac{x_i}{g_m(\mathbf{x})} \right) \right]_{i=1, \dots, D}, \quad g_m(\mathbf{x}) = \left(\prod_{i=1}^D x_i \right)^{\frac{1}{D}} \quad (5.3)$$

While the clr transformation produces a log-ratio for each component and is easy to interpret it has the disadvantage of a singular covariance matrix, which precludes the use of some of the standard statistical tools.

The isometric log-ratio (ilr) transformation, introduced by Egozcue et al. (2003), is related to the clr by a set of $D - 1$ linear combinations of the clr coefficients

$$\text{ilr}_j(\mathbf{x}) = \sum_{i=1}^D \beta_{ij} \text{clr}_i(\mathbf{x})$$

in such a way that the vectors of coefficients $\beta_j = [\beta_1, \beta_2, \dots, \beta_D]$ are orthogonal by pairs, and they are all normalized to length $1 = \beta_1^2 + \beta_2^2 + \dots + \beta_D^2$. The advantage of an ilr transformation above the clr transformation is that the covariance matrix can be inverted, which is required by most of the statistical tools used in this dissertation. The disadvantage of ilr values is that they are in general difficult to interpret.

One way of producing an interpretable ilr transformation is to use one special case of ilr, the so called balanced log-ratios (Egozcue and Pawlowsky-Glahn 2005; Parent et al. 2013). A balanced log-ratio is the log-ratio contrast between two non-overlapping subcompositions of one composition. It is expressed as the normalized quotient between the geometric mean of one subcomposition of elements against the geometric mean of a second subcomposition of elements. With the first subcomposition $\mathbf{r}$ containing D_r elements and the second subcomposition $\mathbf{s}$ containing D_s elements, the balanced log-ratio is calculated by:

$$[r_1, \dots, r_{D_r} | s_1, \dots, s_{D_s}] = \sqrt{\frac{D_r \cdot D_s}{D_r + D_s}} \cdot \ln \left(\frac{g_m(\mathbf{r})}{g_m(\mathbf{s})} \right) \quad (5.4)$$

Another way to make ilr transformed data interpretable is calculate the ilr by a known vector space base, e.g. as used for the ilr-ANOVA in Section 5.3.

5.2. Vratios ²

For certain questions not only the concentration data are used but also the ratios of element concentrations between two samples, like $K_{sample1}/K_{sample2}$ for the element Potassium. To avoid ambiguities with ratios of parts within one sample composition, for example between two elements of one sample $K_{sample1}/P_{sample1}$, we will call these ratios between two samples 'vratio' (vector-ratio). These vratios are calculated for example to describe uptake of elements through plants by the vratio plant/soil, translocation of elements within a plant by the vratio leaf/root, the relation between mineral composition versus host rock by the vratios mineral/rock, etc.

This simple approach of dividing one composition by the other describes the proportion of one element concentration between two samples and is for some research questions a good and correct approach. However, this approach might lead to biased conclusions or blurred results if the focus is laid upon the relation between elements of vratios: The simple vratios, being ratios of intrinsically linked proportions, are affected by the constraints of compositional data (e.g. Duce et al. 1975; Reimann and Caritat 2000). Especially if statistical tools like principal component analysis (PCA), linear discriminant analysis (LDA), analysis of variance to create an ilr-base (ilr-ANOVA), clustering, biplots, etc. are used to explore relations between multiple variables of vratios, the results can be affected by the untreated skewness of the distribution of vratios, the chosen subcomposition of variables, or by one or more dominating variables.

In order to reduce the biases, support visibility of trends or correlations or to allow quantification of trends vratios can be transformed into less skewed and/or unconstrained data. Equivalent to transformations developed for vectors of compositional data the same method of transformations can be used for vratios. One method often used is to normalize each part of a composition to a reference part for calculating the vratio: $vratio_i = \mathbf{x}[x_i]/\mathbf{y}[x_i] \times \mathbf{y}[x_{ref}]/\mathbf{x}[x_{ref}]$ (e.g. Walker 1972; Zoller et al. 1974). The choice of the reference part has to be done with great care and the constraints of each ratio of x_i/x_{ref} for the setting of the study must be taken into account (Duce et al. 1975; Reimann and Caritat 2000).

In this dissertation we will introduce logarithmic vratios, centered vratios and centered logarithmic vratios, equivalent to the additive log-ratio (alr) and the centered log-ratio (clr), introduced by Aitchison (1986) for compositional data vectors. These transformation of data can be seen like applying different 'filters' which could help to see further

²Parts of this section has been presented at Goldschmidt Conference 2017 (Pospiech and Tolosana-Delgado 2017)

aspects and trends in a mutli-variate setting of vratios. The aim, advantages and disadvantage will be described and discussed on the example of ionome of shoot tips compared to the geochemical composition of corresponding soils. These five filters are: the normalization to one reference element, 'ar'-filter, the normalization to the geometric mean, 'cr'-filter, and logarithmic transformation of the simple ratios and these normalizations, 'log', 'alr' and 'clr'- filters.

There are several terms used for the process of elements moving from the soil into plant tissue, like 'element uptake', 'transfer-factors', 'soil-plant partition coefficient', 'bio-concentration factor', 'concentration ratio', 'enrichment factor' or 'biological accumulation coefficient' (Hope 1995; Roca and Vallejo 1995; Dinelli and Lombini 1996; Rodríguez et al. 2002; Tomé et al. 2003; Chojnacka et al. 2005; Reimann et al. 2007; Goni et al. 2014). The definitions may refer to the total content in the soil, to the bio-available element solution, to the total plant, to some specific part of the plant, like stems, fruits, etc, or even to an estimation coefficient in order to predict the uptake of an element by a certain species (Chojnacka et al. 2005). Because this thesis focuses on the element concentration in the plant in respect to the corresponding soil, the neutral, descriptive term plant-soil-ratio is used. For 'soil' the total concentration of either top- or subsoil is used, and for 'plant' the total concentration of either shoot tip or mature leaf is used.

5.2.1. Calculation of Vratio

The simple vratio between two compositions, $\mathbf{x}$ and $\mathbf{y}$, is defined as:

$$\text{vratio} = \left[\frac{x_i}{y_i} \right]_{i=1, \dots, D} = \frac{\mathbf{x}}{\mathbf{y}}$$

If each part of a composition is related to a reference part and vratio are then calculated by these 'normalized' parts, as used by e.g. Walker (1972) and Zoller et al. (1974), in the following it will referred to as representation 'ar' - by analogy to the additive log-ratio without the logarithmic transformation:

$$\text{vratio_ar} = \left[\frac{\frac{x_i}{x_{ref}}}{\frac{y_i}{y_{ref}}} \right]_{i=1, \dots, D} = \frac{\mathbf{x}}{\mathbf{y}} \times \frac{y_{ref}}{x_{ref}}$$

Following the analogy of the definition of 'alr' for compositional data by Aitchison

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(1986), the 'alr' representation will be:

$$\text{vratio_alr} = \left[\ln \left(\frac{\frac{x_i}{x_{ref}}}{\frac{y_i}{y_{ref}}} \right) \right]_{i=1, \dots, D} = \ln \left(\frac{\mathbf{x}}{\mathbf{y}} \times \frac{y_{ref}}{x_{ref}} \right)$$

Normalizing the parts to the geometric mean ($g(\mathbf{x}) = \sqrt[D]{x_1 \cdot x_2 \cdots x_D}$) and then calculating ratios of these 'centered' compositions will be referred to as representation 'cr' (*centered ratio*):

$$\text{vratio_cr} = \left[\frac{\frac{x_i}{g(\mathbf{x})}}{\frac{y_i}{g(\mathbf{y})}} \right]_{i=1, \dots, D} = \frac{\mathbf{x}}{\mathbf{y}} \times \frac{g(\mathbf{y})}{g(\mathbf{x})}$$

Applying the logarithm on the representation 'cr' leads to the representation 'clr' (*centered log-ratio*), analogical to the definition of 'clr' for compositional data by Aitchison (1986):

$$\text{vratio_clr} = \left[\ln \left(\frac{\frac{x_i}{g(\mathbf{x})}}{\frac{y_i}{g(\mathbf{y})}} \right) \right]_{i=1, \dots, D} = \ln \left(\frac{\mathbf{x}}{\mathbf{y}} \times \frac{g(\mathbf{y})}{g(\mathbf{x})} \right)$$

5.2.2. Comparison of Vratio Representations

To visualize the differences between the six representations of vratio calculation, 13 elements had been selected to generate PCA-biplots (Section 5.4) in order to demonstrate the spread of vratics and the relations among them. Figure 5.1 shows on the left side biplots of the non-logarithmic representations, and on the right side the biplots of the logarithmic representations. For the representations 'ar' and 'alr' the element K had been chosen as reference element for illustration, because K is one of the elements which has very different uptake between regions. In the appendix there are further examples with P and Ca as reference element for the representations 'ar' and 'alr' (Figure C.1).

The plots in Figure 5.1 reveal that for this data set all non-log-representations have in general roughly a similar pattern and all log-representations have roughly a similar pattern. Vratios calculated via non-log-representations have very different values and variances, as well between elements as between representations. On the other hand, log-representations have more homogeneous distributed values (Tables 5.1 and 5.2).

Non-log-representations Among the non-log-representations the representation 'simple' gives the factor between the concentration in the first data set compared to the

concentration in the second data set. Table 5.1 displays the medians vratios for eight different representations. In the example data set the element S has highest vratios with median = 19, while La and Fe have lowest vratios, both with median = 0.0016. The element K with vratios of median = 1.2 is in average similarly concentrated in shoot tips as in the corresponding soils. All 'ar' representations are similar between each other, because each 'ar' representation has the same denominator and between the various 'ar' representations only the denominator differs. For the representation 'cr' the homogeneity of this normalization factor is determined by the scatter of the geometric means of both data sets.

The advantages of the non-log normalizations take effect if statistical tools are used which incorporate e.g. the variance of the vratio distributions. For nearly all non-log-representations the variance of the vratios is highest for the elements S and K, only in the representation 'ar Ca' the vratios of P show also notably high variance (Table 5.2). For all other elements the distribution of vratios have minor variances. The coloring by region in the left plots of Figure 5.1 reveal that the regions Arcanjo and Registro have very high variances of plant-soil-ratios for K compared to the plant-soil-ratios for K in Darjeeling and Assam. On the other hand, the high variance of vratios of S is provoked by large differences in plant-soil-ratios within the regions Darjeeling and Assam.

The general pattern of the non-log-representation biplots is similar, except for the representation 'ar K': The component 1 is mainly controlled by the link between S and the origin of the biplot, while the spread of samples along the component 2 is mainly caused by the variance of the vratios of K; this also explains why the biplot of 'ar K' is very different in its pattern compared to all other non-log-representations. Differences between the representations can be seen in the sample grouping, e.g. compare 'simple' vs. 'cr' vs. 'ar Ca' (Figure C.1). Through applying these various mathematical filters the differences of the representations visually highlight different distributions of the respective elements. For example, in the plot of representation 'simple' it becomes clear that the K - uptake in shoot tips in Brazilian tea gardens differs notably compared to the K - uptake in Indian tea gardens and the K - uptake differs between the Brazilian regions, too. Additionally, within the Brazilian sample group there is a slight offset between the regions parallel to the component 1 axis (Figure 5.1, left side, method 'simple' and method 'cr'). This suggests that differences in K - uptake could be the main parameter which discriminates the various regions in Brazil, but not the only parameter. Of the displayed non-log-representations it is indeterminable which else vratios distinguishes between the regions. The biplots suggest that a further investigation on Sr or Rb uptake could

5. Mathematical Tools

lead into more satisfying results. Another example of how a different normalization may help to find trends and discrimination parameter can be seen in the biplot of representation 'ar Ca' (upper left plot in Figure C.1). In this plot most samples from Assam form a distinguished group, and, by the position of the variable labels, presumably the S/Ca and P/Ca ratios in soils and shoot tips are important proxies. The interpretation of this plot could be: The content of P in leaves compared to P in soil is, compared to the ratio of Ca in leaves to Ca in soil, higher for Assam than in the other regions.

Log-representations The log-representations have the advantage that through the logarithm the spread of data is more comparable between values of different orders of magnitude. Hence, the approach of using a log-representation helps to see differences in vratio of generally very small values compared to vratio of other variables in the data set. Table 5.1 displays the difference in orders of magnitude: The medians of vratio of non-log-representations span up to five orders of magnitude, while the values of log-representations have a much smaller range. Accordingly, the variances of log-representations also span less order or magnitudes (Table 5.2).

The general pattern of log-presentation biplots is similar for the methods 'log', 'alr K' and 'clr' (Figure 5.1, right side), but are slightly different for the methods 'alr Ca' and 'alr P' (Figure C.1). As discussed for the non-log-representations, the variance of vratio involving the element K discriminates between Brazilian and Indian regions. Only for the method 'alr P' (Figure C.1) samples from the region Registro cannot be clearly separated from Indian sample groups. In contrast to the non-log-representations, the biplots of log-representations allow a clear discrimination of sample groups of the regions within India and Brazil: For nearly all filters samples from Darjeeling, Assam, Araucária, Arcanjo and Registro plot in distinguished groups. Only samples of Araucária and Arcanjo are indistinguishable for certain log-representations, like 'clr' and 'alr Ca'. Similar to the non-log-representations, each log-representations reveals a slightly different aspect of the sample set.

As a visual tool the biplots of the log-representation reveal following results: i) all regions are different from each other concerning element uptake pattern, because for several filters the samples group by regions. This could not be seen as clearly from the non-log-representation biplots. ii) K - uptake is one the main differences between Indian and Brazilian samples. This could be seen more clearly for the non-log-representations. iii) Various other details, e.g. tea in Assam has the lowest Ca and Al - uptake, tea in Registro shows the highest Sr - uptake, the uptake of Ni and Fe does not discriminate

between the regions, etc.

In summary, the log-representations show less clearly the main players of differences in *vratios* of a data set, but rather reveal the spread of *vratios* of small values in a data set. The choice of representation depends upon the question: For example, if the focus of the visual approach should be laid upon differences of the uptake of Ca by tea in various regions, the representation 'alr Ca' (Figure C.1, upper right plot) displays that tea in Assam, Araucária and Arcanjo has less uptake of Ca than tea in Registro and Darjeeling.

5.2.3. Summary

Vratios (vector-ratios) are element-wise ratios between two samples. There are six different options of representing *vratios*, the simple ratio, a ratio normalized to one element, the ratio normalized to the geometric mean and the three corresponding logarithmic representations. Each representation focuses on different aspect of the data set of *vratios*. The choice of a representation depends vastly upon the question asked for the specific data sets. Generally, non-log-representations emphasize on the *vratios* of great values and high variance. On the other log-representations are less sensitive to the total spread of data and allow to see spread of *vratios* of different orders of magnitude. Especially the representation of *clr-vratios* proved to be a very handy tool for a first exploratory approach. For the visual exploration of the *vratio* data sets biplots based on PCA transformation are a powerful tool to identify possible trends for further statistical analysis.

Table 5.1.: Median of vratios of six different representations. Table displays only selected elements. Each median is calculated by 106 vratios.

Method	Al	Ca	Co	Fe	K	La	Mg	Mn	Ni	P	Rb	S	Sr
simple	0.0076	2.9	0.0096	0.0016	1.2	0.0016	0.37	0.59	0.21	6.2	0.36	19	0.42
ar K	0.0056	1.9	0.0062	0.0011	-	0.00094	0.26	0.42	0.15	4.4	0.24	13	0.24
ar Ca	0.003	-	0.0032	0.00061	0.54	0.00054	0.17	0.23	0.093	2	0.13	5.8	0.15
ar P	0.0012	0.5	0.0016	0.00025	0.23	0.00029	0.063	0.1	0.035	-	0.069	2.6	0.082
cr	0.038	15	0.046	0.0079	7	0.0081	2	3.3	1	32	2	89	2.1
log	-4.9	1.1	-4.6	-6.4	0.18	-6.5	-1	-0.53	-1.6	1.8	-1	2.9	-0.88
alr K	-5.2	0.62	-5.1	-6.8	-	-7	-1.3	-0.87	-1.9	1.5	-1.4	2.6	-1.4
alr Ca	-5.8	-	-5.7	-7.4	-0.62	-7.5	-1.8	-1.5	-2.4	0.7	-2	1.8	-1.9
alr P	-6.7	-0.7	-6.4	-8.3	-1.5	-8.1	-2.8	-2.3	-3.4	-	-2.7	0.96	-2.5
clr	-3.3	2.7	-3.1	-4.8	1.9	-4.8	0.72	1.2	0.015	3.5	0.7	4.5	0.74

Table 5.2.: Variance of vratios of six different representations. Table displays only selected elements. Each variance is calculated by 106 vratios.

Method	Al	Ca	Co	Fe	K	La	Mg	Mn	Ni	P	Rb	S	Sr
simple	5.2e-05	21	7.6e-05	3.7e-06	110	1.6e-05	1.5	1.9	0.016	11	0.9	540	0.54
ar K	2e-05	4.8	5.7e-05	5.8e-07	-	1.7e-06	0.01	0.083	0.016	8.4	0.032	500	0.073
ar Ca	1.6e-05	-	0.00015	1.1e-06	20	1.2e-05	0.29	0.51	0.011	30	1	570	0.016
ar P	1.9e-06	0.28	4.5e-06	8.3e-08	3.2	8.4e-07	0.053	0.095	0.0014	-	0.056	18	0.008
cr	0.00044	130	0.0018	1.4e-05	390	0.00015	4.1	7.5	0.34	240	6.4	15000	2.2
log	0.27	0.94	0.48	0.4	1.5	1.1	0.84	0.54	0.33	0.28	0.86	0.83	0.75
alr K	1.7	1.6	1.6	1.1	-	1.2	0.23	1	1.4	1.4	0.45	3	1.1
alr Ca	0.67	-	1.7	0.99	1.6	1.9	1.1	1.3	0.85	0.93	1.7	1.7	0.37
alr P	0.54	0.93	0.72	0.48	1.4	1.5	0.82	0.82	0.53	-	1	0.66	0.99
clr	0.32	0.65	0.53	0.23	0.71	0.79	0.31	0.35	0.28	0.3	0.47	1.1	0.42

Figure 5.1.: Biplots of the PCA of vratios between shoot tips of *C. sinensis* and corresponding soil analysis for six different representations. Left side of the plot are all non-log-representations, on the right side of the plot are the corresponding log-representations. Labels of elements do not overlap for visibility.

5.3. Statistical Tools

This section gives an overview of the statistical tools used for the multivariate data in this thesis. Detailed explanations of the principles of HCA, PCA, LDA and ANOVA can be found for example in Fahrmeir and Hamerle (1984).

Hierarchical cluster analysis

For the agglomerative hierarchical cluster analysis (HCA) a measure of dissimilarity between sets of observations is used to calculate which groups or individual observations are most similar and can be merged into one group. The dissimilarity between observation can be expressed for example as the distance between observations, which can be calculated by various methods. Starting from each of the D observations being an individual group the groups are incrementally merged into bigger groups. The results of the clustering are displayed as dendrograms. In this thesis all HCA are calculated with the R-function `hclust` of package 'stats' with the method `ward.D2`, which implements Ward's (1963) clustering criterion (Murtagh and Legendre 2014). At every agglomeration step, the `ward.D2` clusters the two groups which produces a minimal loss of homogeneity through the merging. The algorithm calculates the loss of homogeneity by subtracting the sum of total variances within each group before merging from the variance of the group after merging (Boogaart and Tolosana-Delgado 2013).

Principal component analysis

A principal component analysis (PCA) is used to find associations between variables through reducing the dimension of the data set: The data are projected into a new coordinate system by an orthogonal linear transformation. The first coordinate (first principal component) of this coordinate system points along the greatest variance of the observations, the second coordinate (second principal component) along the second greatest variance and so on. In this thesis the PCA is calculated from the R-function `princomp` of package 'stats' which derives the new coordinate system by using the eigenvalue decomposition. For `princomp` the columns in the matrix 'loadings' contain the eigenvectors while the 'scores' are the coordinates of the individuals (observations) projected onto the principal components.

If a PCA is used for concentration data the PCA is always applied on clr-transformed compositions. This transformation is the best choice for PCA due to its inherent prop-

erties and because results are intuitively interpretable based on the scores for each original variable.

Linear discriminant analysis

The linear discriminant analysis (LDA) is a technique based on singular value decomposition to find a coordinate system which maximizes the variance between categories and minimizes the variance within categories. It is used to distinguish groups of samples by a categorical variable, e.g. the region of sample origin. The LDA is calculated from the function `lda` of the package 'MASS'.

Analysis of variance to create an ilr-base

Generally, ANOVA denotes a regression-like technique where the covariables are of categorical type. For complying the necessities of compositional data the linear regression model is applied on log-ratio transformed element data, e.g. *ilr* (Eq. 5.1), with categorical covariables. In this thesis the built-in ANOVA function of R is used to create an *ilr*-base with a specific structure which captures the grouping of element variables in relation to the categorical variable: By means of the regression model the total variance of the data set is decomposed in the variance due to the differences between group means and the variance within each group. This very specific application of ANOVA technique is used as an exploratory tool to assess whether groups of samples have similar or different behavior within a certain subcomposition of elements.

The *ilr*-ANOVA is calculated from the R-function `lm` of package 'stats' with `lm(x~g)`, *x* being the *ilr* transformed concentration data and *g* begin the categorical variable. The resulting *ilr*-coefficients are converted into *clr*-coefficients, and, based on these, a new *ilr*-base is calculated. The structure of this new *ilr*-base is visualized by dendrograms from the function `CoDaDendrogram` of the package 'compositions'. For more detailed explanation please refer to Tolosana-Delgado and et. al. (2019).

5.4. Visualization Tools

Biplot

Biplots (Gabriel 1971, 1972) are one possibility to visualize a multivariate data set in one plot. In a classical biplot the plot is based on a PCA (Section 5.3) of the variables.

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The biplot is a scatter plot of two coordinates of the PCA, generally the first coordinate versus the second coordinate. The loadings of `princomp` are plotted as arrows or labels of the variables and the scores of `princomp` are plotted as dots or labels representing the observations which are projected onto the coordinate system of the two PCA-components.

The classical PCA-biplots are row-metric-preserving, so-called “form biplots” (Greenacre 2010): The length of the arrows approximates the variance of each element variable. The angle between two arrows approximates the correlation between two elemental scores.

In biplots based on log-ratio transformed data the rays are seldom interpretable and one should focus instead on the links between apexes which represent the log-ratio between two elements. The length of a link will be proportional to the variance of the log-ratio of the two variables involved. Two orthogonal links will indicate uncorrelated data respectively parallel links will indicate good correlation between the log-ratios of the several pairs of elements affected (Aitchison and Greenacre 2002; Greenacre 2010).

Dendrogram

Dendrograms are hierarchical, tree-like graphs to illustrate clustering and/or grouping of samples or variables. In this thesis two different types of dendrograms are used:

HCA dendrogram Dendrograms illustrating the result of an HCA, which is the result of the R-function `plot.hclust` of the package ‘stats’.

CoDa dendrogram Dendrograms illustrating the hierarchy of groups underlying the *ilr* structure determined by the *ilr*-ANOVA (Section 5.3). These graphs are produced from the R-function `CoDaDendrogram` of the package ‘compositions’: Each horizontal axis represents one coordinate of the vector field of an *ilr*-transformed data set (Section 5.1) and the contact point the coordinate mean. The length of the vertical bars are representing the variance of the specific elements or element subcompositions.

Heatmap

A heatmap is a visualization tool to simultaneously show the similarity or associations between the rows and between the columns of a matrix. In this thesis heatmaps are used to answer two questions:

1. For which pairwise log-ratios is the distribution of data set A similar to the pairwise log-ratio distribution of data set B?
2. Which groups of elements have similar log-ratio distributions between data set A and data set B?

To answer the first question the distributions of the pairwise log-ratios of data set A and data set B are compared via tests for equal means of two distributions. These are, depending on the sample sets A and B, either the Student's *t*-test, Wilcoxon signed rank test or Mann-Whitney test. The heatmap is a map of tiles with each tile colored by the probability value (p-value) of the respective test: p-values below 5% (hypothesis is rejected) are colored reddish, and p-values above 5% (the means of the log-ratio distributions are considered as equal) are colored blueish.

To answer the second question the elements are grouped by their pairwise log-ratio p-values. The grouping is calculated from `distfun(X) %>% hclustfun %>% as.dendrogram` of package 'stats', whereof X is the matrix of p-values.

6. Correction for Adhering Particles

Plants grown in open field, such as tea, are prone to also contain adhering particles, such as airborne dust or spluttered soil particles. During digestion and analysis of the samples adhering particles (AP) alter the elemental composition of the plant material and introduce a bias on the tea's ionome. The amount of adhering particles on tea might vastly differ due to local climate conditions, e.g. frequent raining versus longer period of dryness or wind, distance to road or a track across fields and local manufacturing conditions, e.g. whether a filter is placed in front the factory's air intake tube. But processed tea cannot be washed or cleaned prior to analysis because it is already steamed, dried, milled or otherwise processed. To make the sample group of processed tea and plucked leaves better comparable between seasons, regions and manufacturing conditions a correction for adhering particles (correction for AP) should be calculated.

The method of the correction for AP was developed on a data set of 1040 plant samples grown in open field and pot trials in Germany. Accordingly, the Section 6.1 contains data of field plants from several projects conducted by Benedikt Sauer, Wiebke Fahlbusch, Tino Pasold and Hans Ruppert. The application of the method on tea data is presented in the Sections 6.2 and 6.3.

6.1. Method ¹

Exact and reproducible analysis of element concentrations in plant tissue is the basis for many research fields such as environmental, health, phytomining, agricultural or provenance studies. Unfortunately plant samples collected in the field will always contain particles on their tissue surfaces such as airborne dust or soil particles (Chamberlain 1983; Harrison and Chirgawi 1989; Faucon et al. 2007). If not removed these particles may induce a bias to the element concentrations measured in plant samples. The influence of adhering particles on element concentration in plants is negligible for elements

¹ This section was published in Solveig Pospiech et al. (2017). Alteration of trace element concentrations in plants by adhering particles – Methods of correction. *Chemosphere*, 182, 501–508

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which have a much higher concentration in the plant tissues compared to the adhering material. This is the case for most main or minor nutrient elements such as P, K, Ca, Mg, S, Mn, B, Mo, Zn or Cu (Arkley et al. 1960; Mitchell 1960; Bargagli et al. 1995). But elements with typically very low concentrations in plant tissue such as Al, Co, Fe, Li, Ni, Ti, Sc, Zr, or REEs, may show significantly altered concentrations measured in the plants due to adhering particles. Mitchell (1960) proposed that elements with concentration ratios of soil to plant above 100 might show biased concentrations in the measured samples.

Reducing the impact of adhering particles on trace element concentration in plants is crucial in order to be able to compare elemental composition of plants, e.g. between sampling periods or slightly different sampling methods (MacNaoidhe 1995), or for biomonitoring studies. It is also important in studies for plant nutrition to calculate the real uptake of an element by a plant, e.g. for phytoremediation/phytomining (Baker et al. 1994; Fässler et al. 2010; Wiche et al. 2016), or in studies on the trace elements Co, Ni, Mn and Mo which are required by the microorganisms in biogas plants (Sahm 1981; Demirel and Scherer 2011).

Most authors recommend washing or carefully rinsing of the plant material to clean the samples prior to analysis. Washing methods were tested by several authors, e.g. ultra-pure water, washing detergents, complexing agents like EDTA, slightly acidic solutions or combinations of these (Husted et al. 2004; Faucon et al. 2007; Cook et al. 2009). The disadvantages of the washing method are (1) particles may remain in leaf axils or on rough foliar (or epidermal) surfaces of the plants (Cook et al. 2009) and (2) elements may get leached from the plant tissue. Washing is sometimes not possible if the plant material was already processed prior to sampling, e.g. by fermentation, drying, cutting or mixing.

Although several authors were aware of the problem of irremovable adhering particles and their bias to trace element concentrations in plant tissue (Mitchell 1960; Tölgyesi and Nagy 1990; Markert 1995; Reimann et al. 2001; Anke and Seifert 2004; Faucon et al. 2007; Verbruggen et al. 2009; Censi et al. 2017), or showed by experimental studies the influence of adhering particles on plant tissue (Cary 1992; Gerzabek et al. 1992), only Bargagli et al. 1995 and Sauer and Ruppert 2013 provided a mathematical approach using aluminum or titanium as a reference element to estimate the amount of adhering material and calculate "true" element concentrations in plant tissue.

Based on the model that the analyzed plant material is a mixture of plant tissue and a very minor amount of adhering particles we developed more general methods to calcu-

late a correction term for adhering material. We will present three methods of calculating a correction term and show the effect of these correction terms on the trace element concentrations of plant matter.

6.1.1. Materials and Methods

Study Sample Set

The sample set consist of plants and corresponding soil samples from different research projects between 2011 and 2015. In all projects a broad element range was measured focusing on trace elements. The plants in these studies comprised forage and energy crops (for biogas production), perennial and catch crops (Table 6.1). In this study the element data of a total of 1040 plant samples of 19 species and at least 10 samples for each species is presented.

Table 6.1.: List of plants in the data set used for correction for adhering particles.

Plant Species	Scientific name	Nr. of samples	Nr. of locations
Amaranth	<i>Amaranthus</i> spp.	255	12
Barley	<i>Hordeum vulgare</i> L.	11	2
Beet (leaves)	<i>Beta vulgaris</i> L.	18	7
Buckwheat	<i>Fagopyrum esculentum</i>	47	16
Catnip	<i>Nepeta cataria</i> L.	14	11
Cup Plant	<i>Silphium perfoliatum</i> L.	13	8
Faba Bean	<i>Vicia faba</i> L.	59	11
Maize	<i>Zea mays</i> L.	151	23
Mustard	<i>Sinapsis alba</i> L.	15	12
Oat	<i>Avena sativa</i> L.	24	2
Pea	<i>Pisum sativum</i> L.	14	3
Quinoa	<i>Chenopodium quinoa</i>	50	16
Rye	<i>Secale cereale</i> L.	102	20
Ryegrass	<i>Lolium perenne</i> L.	28	4
Sorghum	<i>Sorghum bicolor</i> L.	13	3
Sunflower	<i>Helianthus annuus</i> L.	52	14
Triticale	<i>Triticosecale</i> Wittm.	92	19
Vetch	<i>Vicia villosa</i> L.	55	6
Wheat	<i>Triticum aestivum</i> L.	27	15

6. Correction for Adhering Particles

The plant and soil samples were retrieved from open arable field trials and from (open) pot trials filled with differently soils. Of the 1040 plant samples 789 plants were from open field (20 locations in southern Lower Saxony and Bavaria, Germany), and 251 from open pot trials (a total of 13 different locations in Lower Saxony). The pots were located close to the sedimentology and environmental geology department of the Georg-August University in Göttingen. None of the plant samples were rinsed. The soil types in the field ranged between silt, silty loam and sandy loam with a pH of 5.8 to 7.0 (measured in 0.01 mol/L CaCl_2).

Sampling, Sample Preparation and Analysis

The plant samples were cut at ca. 10 cm above soil surface at the stage of lactic ripeness or end of flowering. The roots are not included in the analysis. About 500 g of soil samples were taken in the upper part of the soil (up to 30 cm depth) and are air dried and sieved to < 2 mm in grain size. All samples, soils and plants, were dried at 105°C. A minimum of 100 g of the soils and ca. 500 g of plants were ground in an agate ball mill to avoid metal contamination.

Aliquots of 150 mg of soil respectively 700 mg of plant powder were fully digested with a mixture of ultra pure concentrated HNO_3 , HClO_4 and HF in closed ultra clean PTFE vessels (PicoTrace, Bovenden, Acid sample digestion system DAS 30). In the soil samples a small amount of HCl is added. Soil samples were diluted to 100 ml the plant samples to 50 ml for measurement. In the resulting clear sample solutions 47 elements could be quantified by ICP-OES and ICP-MS.

To ensure clean handling and quality of analysis for every 30 samples one to two blank solutions and one or two international reference standards were digested and analyzed together with the samples. For plant samples the following international reference materials were used: GBW 10052, BCR-129, WEPAL-IPE-126, WEPAL-IPE-168. For soils the geochemical standard TW-45 was used. Results were only accepted if concentrations were above the limit of detection (3-fold standard deviation of the blank concentrations for each analysis batch) and if the corresponding reference samples showed concentrations within the certified values. Average precisions for the elements were better than 5% for all main elements and most of the trace elements; for plants the ultra-trace elements Cr, Co, Mo, Sn, and the heavy REE showed average precision between 10% - 20%. All concentration data are given in *mg/kg d.w.*.

6.1.2. Theory of the Correction

All correction terms are based on the following simplified model: The plant samples collected from open field trials (**P**) consist of the pure plant material, the ionome (**I**), and a minor content of deposited solid material from different sources, the adhering particles (**A**). With a digestion method ensuring complete and total dissolution of the sample the analytically determined element concentration, **P**, contains both components, **I** and **A**. Hence the concentrations of the ionome **I** could be calculated by subtracting adhering particles **A** from the analyzed plant sample **P** (Eq. 6.1).

The most important sources of adhering particles are airborne dust, soil particles from wind or rain splash. In this study the adhering particles are assumed to be mainly soil particles (**S**). Especially the lower parts of plants will be strongly affected by splashed soil particles, but this holds also for the higher parts of the plants even if less affected.

We are aware that a fractionation of soil particles may occur during transport through the air or that collected atmospheric dust could locally be a better proxy for adhering material, but to simplify our calculations we take into account only data of the soils corresponding to the plants. Air dust collection and analysis would be extremely laborious and time-consuming.

The content of adhering particles can be approximated by elements with good analytical precision and accuracy and with negligible uptake by plants, hence concentrations approach zero, but high concentrations in the adhering particles. We call these elements "indicator elements", e.g. P_{ind} , S_{ind} or A_{ind} . In order to estimate the content of adhering soil k (Eq. 6.1) to the plant samples we propose three different methods:

Method 1: Using one pre-defined element indicator element for calculating the content of adhering particles in plant samples From all elements fulfilling all requirements of one indicator element chosen to calculate k in Eq. 6.4 (Ti, Al, Zr, Sc...). For example using Ti as indicator the content of **A** is calculated through $k = P_{Ti}/S_{Ti}$ and this k is then used in Eq. 6.2. Resulting negative concentrations should be set to zero.

Method 2: Subtracting the smallest possible content of adhering particles (smallest k) For each sample the element with the smallest k of all ratios $k = P_i/S_i$ of each sample is taken as indicator element, hence every sample is corrected based on a different i . With this method only the smallest possible content of **A** is subtracted from

6. Correction for Adhering Particles

P (Eq. 6.2). Typical indicator elements are Ti, Al, Th, Cs, Zr etc., if they can be measured with high sensitivity and reproducibility. With this method there are no negative concentrations.

Method 3: Using the median of several elements with a very small k for calculating the content of adhering particles In order to reduce the uncertainty of the content of adhering particles based on only one element as in method 1 and 2 an average of several k of indicator elements can be calculated. With Δk being the absolute error of k we suggest to take the median of the k of all elements which values $k - \Delta k$ are smaller than $k_{smallest} + \Delta k_{smallest}$. The value of the median $\bar{k}$ is then used as k in Eq. 6.2. Negative concentrations should be set to zero, because statistically the k of all elements, which error overlaps the error of the element with smallest k , are indistinguishable. For the same reason, all elements contributing to the computation of the median $\bar{k}$ should be set to zero, because these small values should not be interpreted.

6.1.3. Calculation of the Correction

With k as the variable for the content of **A** in **P**, $0 < k < 1$, the composition of **P** can be expressed as the sum of **I** and **A**:

$$\mathbf{P} = \mathbf{I} \cdot (1 - k) + \mathbf{A} \cdot k \quad (6.1)$$

Resolving equation 6.1 for **I** results in equation 6.2:

$$\mathbf{I} = \frac{\mathbf{P} - k \cdot \mathbf{A}}{1 - k} \quad (6.2)$$

of which the composition of **A** and the content of the adhering particles, expressed as k , are unknown and assumptions have to be made.

Assuming that the concentration of one of the indicator elements in **I** is zero, $\mathbf{I}_{ind} = 0$, equation 6.2 can be used for solving k , the content of **A**:

$$\mathbf{I}_{ind} = \frac{\mathbf{P}_{ind} - k \cdot \mathbf{A}_{ind}}{1 - k} = 0 \quad (6.3)$$

$$k = \frac{\mathbf{P}_{ind}}{\mathbf{A}_{ind}} \quad (6.4)$$

Note that for the calculation of k only elements of the group of indicator elements are

allowed. Otherwise the correction term will lead to unrealistic element concentrations in **I**.

The absolute error of k , Δk , is calculated through the general formula for error propagation for random and uncorrelated errors of **P**, with $\Delta \mathbf{P}$ as the absolute error range for analyzed plant values, and **A**, $\Delta \mathbf{A}$ as the absolute error range of the adhering particles:

$$\begin{aligned}\Delta k &= \Delta \mathbf{P} \cdot \frac{\partial k}{\partial \mathbf{P}} + \Delta \mathbf{A} \cdot \frac{\partial k}{\partial \mathbf{A}} \\ &\approx \Delta \mathbf{P} \cdot \frac{1}{\mathbf{A}} - \Delta \mathbf{A} \cdot \frac{\mathbf{P}}{\mathbf{A}^2}\end{aligned}\quad (6.5)$$

To estimate the absolute error $\Delta \mathbf{P}$ we use the relative standard deviation of more than 30 measurements of the international reference sample GBW10052 as relative error $\delta \mathbf{P}$: $\Delta \mathbf{P} = \delta \mathbf{P} \cdot \mathbf{P}$. To simplify the error calculation $\Delta \mathbf{I}$ for equation 6.6 we suggest to use in the error-equation as $\Delta \bar{k}$ the standard deviation of $\bar{k}$.

For the results we used Method 3 explained in theory part. We assume that the major source of adhering particles are particles of the soil on which the plants grew ($\mathbf{A} = \mathbf{S}$). Hence based on equation 6.2 the correction equation is

$$\mathbf{I} = \frac{\mathbf{P} - \bar{k} \cdot \mathbf{S}}{1 - \bar{k}} \quad (6.6)$$

If an element has a low concentration in the soils the term $\bar{k} \cdot \mathbf{S}$ becomes close to zero. With $\bar{k} \cdot \mathbf{S} \approx 0$ and the term $\mathbf{P}/(1 - \bar{k})$ being always larger than **P** this may result for main elements in plants into higher concentration in these elements after correction.

6.1.4. Results and Discussion of the Method

Discussion of the Methods

Calculating the content of adhering particles via Method 1 The advantage of the method with a pre-defined element is a rather easy calculation because for all samples the same indicator element is used. The disadvantage is that an overcorrection may occur if the chosen indicator element has a notable higher **P/S**-ratio than the smallest ratio. That might be the case if due to fractionation of the **A** the chemical composition of the adhering particles is not exactly the same as the chemical composition of **A** used in the correction term or if the indicator element is (unexpectedly) taken up by a plant. This is the case for Al in buckwheat *Fagopyrum esculentum* or in tea *Camellia sinensis* (Flaten 2002; H. P. Carr et al. 2003; Zheng et al. 1998). Even Ti, considered as highly immobile in soils, might be taken up by plants in very small quantities and by some

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authors is considered as beneficial to plants (Dumon and Ernst 1988; Cigler et al. 2010; Haghighi et al. 2012).

Calculating the content of adhering particles via Method 2 Subtracting only the smallest possible content of adhering particles minimizes the risk of overcorrection. Disadvantageous is that the correction depends on one element only (lowest ratio of $\mathbf{P}/\mathbf{S}$) and not on analytical reasoning. If the chosen element is an (ultra-)trace element with concentrations close to the detection limit with poor reproducibility and high analytical uncertainty, this results into a high uncertainty of the smallest k and that directly determines the uncertainty of the applied correction.

The content of subtracted $\mathbf{A}$ can therefore vary strongly on the set of trace elements considered for the group of indicator elements. For example plants contain very low concentrations in Hf and therefore it is difficult to determine Hf with high accuracy and precision. If Hf represents the smallest k and Ti second smallest k but considerably higher, the content of $\mathbf{A}$ would be calculated by Hf. If Hf is excluded from the group of indicator elements due to analytical reasons, the content of $\mathbf{A}$ would be calculated by Ti and would result into a stronger correction. So the calculated content of $\mathbf{A}$ would depend upon if Hf whether included to the group of indicator elements or not. Additionally if the indicator element has large errors, these will propagate through the correction to all elements.

Calculating the content of adhering particles via Method 3 This method is particularly interesting if several elements of the group of indicator elements had been analyzed with very small analytical uncertainties. The value of $\bar{k}$ is based on several elements with overlapping error Δk_i . That avoids on the one hand the problem of method 1 that the element might be taken up by the plant and on the other hand avoids the problem of method 2 that it is quite random which element is the element used for correction and that the analytical error might be quite high. The disadvantage is that the implementation of method 3 on a routine basis is not as simple as for example in method 1, especially if error calculation is included.

Evaluation of the Calculated Content of Adhering Particles

The content of adhering particles in $\mathbf{P}$ had been calculated via method 3 for 1040 whole crop samples from fields in Germany. As shown in Figure 6.1 proportions of adhering

particles vary among samples on the range between 0 wt% (no particles) and 6.1 wt%, with median values of about 0.09 wt% in the pot trials and 0.16 wt% in open field trials.

Although the content of adhering material seems to be rather small in comparison with the dry weight mass of the plant samples, it may have a notable impact on many elements. For each sample and for each element the ratio of corrected values to measured values (I/P) are calculated, hence for each element there are over 1000 ratios. The distribution of ratios for each element after applying method 3 is displayed in Figure 6.2. Figure 6.2 shows that - as expected - the concentrations of most nutrients, S, P, Ca, K, Mo, Mg, Zn, Cu, and some trace elements with chemical characteristics analogous to a nutrient, such as Cd, Sr (analogous to Ca) and Ba, Rb (analogous to K), are only slightly affected through adhering soil particles with ratios close to 1 (Figure 6.2).

Figure 6.1.: Distribution (bin width = 0.02) of wt% of adhering soil particles in 1040 crop samples grown in open field ($n = 789$) and open pot trials ($n = 251$). The content of adhering particles calculated via method 3. Right skewed distribution shows that all samples contain at least minor amounts of adhering particles. The median of adhering particles in open field is bigger (dotdash line) than in open pot trials (dashed line) maybe because of severe weather events. The plot is cut at 1 wt%, the maximum value of 6.1 wt% not shown.

The strongest impact of adhering particles is on the trace elements Y, Li, La (representative for all REEs), U, Nb, Ta, Al, Ti, Sc, Th, Zr and Hf: The concentrations after the correction are clearly less than 50% of the measured value. These elements belong to the typical "indicator elements". For Mn, Ni, Ba, Cr, Sb, Tl, Co, Na, Cs, Pb and Fe the distribution of the ratios shows that the impact of adhering soil particles varies among sample: for some the effect is barely measurable, for others the impact is notable. For example, Fe shows a ratio is significantly smaller than 1 for nearly all samples and half

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of the samples contain less than 64% of the measured concentration after correction. In case of essential trace elements for the microorganisms in biogas plants (Co, Ni, Mn, Mo) (Sahm 1981; Demirel and Scherer 2011) we see a diverse picture: The correction slightly affects the concentration of Mo, because Mo is a micro-nutrient for plants and is fairly mobile in the soil solution (Kaiser et al. 2005). It is taken up easily by the plant so that we observe a negligible correction of the measured values (Median = 1.0) only. The median values of Mn and Ni are reduced by 3% (Mn) and 5% (Ni). Co shows for most samples a significant reduction of concentration after applying the correction. On average the Co concentrations are reduced by 16% (Figure 6.2).

Effect of Correction

There is no direct evidence to assess the correctness of the method. But by looking at the grouping of elements via principal component analysis (PCA) on log-ratios it can be seen that some elements show a different behavior before and after the correction.

In Figure 6.3 the upper plot represents the correlation and variance of log-ratios of the uncorrected plants (data set **P**) and the lower plot of the corrected plants (data set **I**). For the original sample data (**P**, Figure 6.3, upper) the elements Nb, Zr, U, Ti, Al, La, Li, Pb and Sb are lying close together which indicates a correlation between these typical indicator elements. This group of elements forms long links to all nutrient elements, except for Fe and Na, indicating no correlation between the group of indicator elements and the nutrients. The ratio **P/S** of the nutrient Fe lies between the ratios **P/S** of indicator elements and nutrients and also in Figure 6.3 in the data set **P** the element Fe plots between the two groups. That means that the concentration of Fe is notably influenced by adhering soil particles. A similar situation applies to Na.

For the corrected samples (**I**, Figure 6.3, lower) the grouping of elements is notably reduced and the links between elements are generally shorter. Indicator elements plot in one corner of the plot. Especially Zr and Nb show a high variation with respect to all other elements. This suggests that the log-ratios between most indicator elements are still quasi-constant but do not form a distinct group. The nutrients Fe and Na have moved towards the nutrient group indicating that their log-ratios are decoupled from the group of indicator elements. Additionally, the shorter links between elements indicate that log-ratios between all elements are now more constant between all samples: Corrected concentrations should better quantify the mechanisms of element uptake into the plants than concentrations including the bias through contamination by adhering particles.

Figure 6.2.: Distribution of ratios (1040 samples) of I/P (corrected/original) for main and trace elements. Corrected values of I calculated via Method 3. Each dot in element rows represents one ratio so that in each row there are ~ 1040 dots. The dots jitter vertically to reduce overplotting. The median is plotted as label at the position of the median, and rows are sorted by median. For S to Sr the median label is omitted because the median is close to 1. Main elements may show slightly higher concentrations after applying the correction (see explanation for Eq. 6.6). Concentrations of elements which contributed to $\bar{k}$ (see explanation method 3) are set to zero to avoid overinterpretation of these small residual values.

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Figure 6.3.: Covariance biplots of **P** (upper, original) and **I** (lower, corrected) of a principal component analysis of log-ratio transformed (clr) data (712 samples with 29 elements). The proportion of the explained variance is 0.52 for the upper plot and 0.49 for the lower plot. The position of the element labels can be interpreted as follows (Greenacre 2010; Boogaart and Tolosana-Delgado 2013): the link between two element labels represents the log-ratio between these two elements. A short link indicates that the elements have a quasi-constant log-ratio. An angle of 90° at the origin means that the log-ratios of the two elements are uncorrelated. Several samples and elements had to be excluded from this examination because of special circumstances (i.e. heavy metal contaminated locations.) The general pattern of the links between elements remains unchanged by this adaption.

6.2. Results for Tea Plant Data

Tea soils had been used as element concentration for Δ for the calculation of the correction for AP for tea plant samples: An average of tea soil composition had been calculated for each tea garden and tea leaf samples had been corrected with the corresponding tea soil average. If for a tea leaf sample no soil data was available, averaged soil element concentrations of the corresponding region or, if no tea soil data of the respective region was available, the upper crust was used as Δ . Using the method 3 on processed tea and plucked leaf samples there is an average (median) of 0.08 wt% of adhering soil particles in tea (Figure 6.4).

Figure 6.4.: Distribution (bin width = 0.02) of wt% of adhering soil particles in 200 plant samples. The content of AP is calculated via method 3. Right skewed distribution shows that most samples contain at least minor amounts of APs. The plot is cut at 1 wt%, the maximum value of 1.1 wt% not shown. Apart from two shoot tip samples the highest amount of AP, $\Delta > 0.3 \text{ wt}\%$, is found in black tea and mature leaves.

One method for visualizing the effect of the correction for AP is displaying the ratios between original and corrected concentrations in a jitter-plot (Figure 6.5): The plot shows that the effect of correction for AP on main and the trace elements S, P, Ca, K, Mn, Cu, Cd, Sr, Zn, Rb, Mg, and Ni is for most samples very small and can be neglected. The elements which are mainly affected by a correction for AP are in tea are the REE, Li, Fe, Zr, Hf, U, Nb, Ti, Th and Ta (Figure 6.5).

In order to visualize the effect of the correction for AP on the relation of the elements

6. Correction for Adhering Particles

in the tea ionome the log-ratios are plotted by biplots (Figure 6.6). In Figure 6.6 the left plot represents the correlation and variance of log-ratios of the uncorrected tea leaf samples and the right plot of the corrected tea leaf samples. The calculation of the biplots is based on samples of several origins (Table 6.2). The distribution of the sample

Table 6.2.: Number of tea samples in respect of country and region plotted in Fig. 6.6.

Country	Region	N
Brazil	São Paulo	37
Brazil	Paraná	5
India	Darjeeling	155
India	Assam	26
India	Nilgiris	25
Iran		2
Japan	Uji	13
Japan	Shizuoka	10
Japan		1
Nepal	Dhankuta	4
Nepal		7
Sri Lanka		1
Uganda		1

dots in the right biplot in Figure 6.6 shows that the grouping of samples has no visible effect by the origin of samples or whether the samples had been corrected via soil data or upper crust. Samples are in both biplots mainly grouped by the subgroup of the samples, especially the subgroup of the mature leaf samples is clearly distinct from the other samples. The correction for AP does not affect the general grouping of samples.

On the other hand some element ratios are visibly affected by the correction for AP: For the original sample data (Figure 6.6, left) the nutrient and micro-nutrient elements K, P, S, Mg, Zn, Cu, Co, Ni and trace element Rb are lying close together which indicates a correlation between these elements. Trace elements Ti, Nb, U, Cr, Zr, Pb and Sb, all elements affected by correction for AP, are loosely plotting in one group which is in the biplot located opposite to the nutrient group. Between these two groups plot the element Fe plots in line with Zr and Ti, which hints a correlation between the pairwise log-ratios of Ti, Zr and Fe. A third group is composed of the elements Ca, Sr, Ba, Tl, Mn and Cd. The group of Sc, La, Y, Al and Li is placed in the field of vastly spreading mature leaf samples.

For the corrected samples the right plot in Figure 6.6 exhibits a slightly different relation between the elements. The shorter links between some elements indicate that the

log-ratios between these elements are more constant for the corrected tea data. For example in the corrected data (right plot) Fe plots closer to the group of nutrients, Ba, Sr and Ca are now in-line hinting a correlation between the elements, and Sc - a typical indicator for adhering soil, plots in a close group with Al, La and Y, which are typical for mature leaves. In general the distance between the group of nutrients, which stay unaffected by the correction, and the group of elements, which are intensely affected by the correction, is smaller after the correction for adhering particles.

For displaying the difference in grouping of elements before and after the correction for AP the method HCA is used (Figure 6.7). In both dendrograms there are three main groups of elements. After applying the correction for AP the three groups are:

1. Th, Ta, Hf, Zr, U, Nb, Ti, Pb and Sb
2. Al, La, Y, Sc, and Ca, Sr, Ba
3. Tl, nutrients, micro-nutrients, and elements with nutrient-similar characteristics, such as Rb, Cs and Cd

The first group are elements which are heavily affected by soil AP (Figure 6.2 and 6.5), the second group are elements which are typically influenced by the developmental stage of the leaf (Figure 6.6) and the last group are the mainly nutrients. Through the correction for AP the elements Fe, Na, Cd and Mn move into the third group, Cr moves out of the first group and Sb and Pb into the first group. Hence, after the correction for AP the element groups are better explainable by plant physiology, such as nutrients vs. non-nutrients, leaves development stages, etc.

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Figure 6.5.: Distribution of ratios (200 tea leaf samples) of I/P (calculated ionome/original) for main and trace elements. Corrected values of I is calculated via Method 3. Each dot in element rows represents one ratio so that in each row there are maximum 200 dots. The dots jitter vertically to reduce overplotting. The median is plotted as label at the position of the median, and rows are sorted by median. For S to Ni the median label is omitted because the median is close to 1. Main elements may show slightly higher concentrations after applying the correction (see explanation in section 'Method').

Figure 6.6.: Covariance biplots of **P** (left, original data) and **I** (right, corrected data) of principal component analysis of log-ratios transformed (clr) data (200 tea leaf samples with 28 elements). The proportion of the explained variance is 0.38 for the left plot and 0.52 for the right plot. The position of the element labels can be interpreted as follows (Greenacre 2010; Boogaart and Tolosana-Delgado 2013): the link between two element labels represents the log-ratio between these two elements. A short link indicates that the elements have a quasi-constant log-ratio. An angle of 90° at the origin means that the log-ratios of the two elements are uncorrelated.

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Figure 6.7.: Dendrograms of elements of **P** (upper plot, original data) and **I** (lower plot, corrected data) of hierarchical cluster analysis (Section 5.3 and 5.4) of closed compositional data using R-function `acomp` of package 'compositions'.

6.3. Discussion for Tea Plant Data

Tea samples consist mainly in shoot tips which are harvested at waist high level at the tea bushes. These harvested plant parts are only few days to maximum 3 weeks old and, accordingly, had been exposed only comparably short time to airborne dust accumulation. In China a study of 1225 *C. sinensis* and processed tea samples showed that Pb contamination of tea increased with increasing proximity to roads, although leaded gasoline was prohibited 1.5 y before sampling (Han et al. 2006). A washing of samples had nearly no effect on Pb concentration for very young leaves and buds, but up 23% removal for mature leaves and the authors of the study concluded that soil dust is one of major source of APs.

Only mature leaf samples have notably longer duration of exposure, and accordingly can have high amount of APs (Figure 6.4). Processed tea samples may have been contaminated by AP by ventilation during the steaming or the withering process (Jabeen et al. 2015): During the withering process (Section 2.3.3) air, often unfiltered, is pushed for several hours through a thick layer of withering leaves, so that air borne dust remains in the tea leaves on the withering tables. In most factories the ventilation air is sucked in well above ground and therefore it has to be assumed that, apart from machine abrasion, airborne dust makes up the main contribution of AP for processed teas.

The correction's assumption, that the adhering particles are mainly soil particles, is especially for tea leaf samples a rather rough approximation. But in absence of data of airborne dust for each region an average of closely located soil data is considered still as the best approximation for correcting the plant data. This assumption is reinforced by the results of the correction for AP: The element Fe, which should as nutrient only be influenced by uptake of the plant, is after the correction closer to the group of nutrients while not before (Figure 6.7 and 6.5). The element Al, an indicator for the leaves' age (Section 2.1.3), is after correction grouped within the group of Ca, Ba and Sr, which are typically higher concentrated in mature leaves than in shoot tips, while before correction it is grouped with the REEs, represented by La and Y, and Sc. In summary comparing the grouping of elements before and after the correction for AP and the overall smaller variance of the log-ratios of elements strongly indicates that the correction successfully reduced the bias induced by airborne particles on certain elements.

Due to the very rough approximation for the elemental composition of adhering particles the corrected concentrations of the mainly affected elements have to be interpreted with caution. There are three ways of handling the plant data:

6. Correction for Adhering Particles

- a) using original plant data
- b) using corrected values and include uncertainty into the results
- c) exclude elements which are a strongly affected by the correction

Option a) has the disadvantage that local events, such as a period of drought or heavy rain, before sampling might have a major effect on the elemental composition of the specific sample which may cause difficulties to interpret the results. On the other hand the chemical signal of the adhering particles, although it is prone to a certain fluctuation, might also contain information.

Option b) has the disadvantage that the errors and uncertainties have to be calculated or estimated and are very high for certain elements. In a second step the errors have to be incorporated into all statistical tools used for the analysis. As a consequence the estimation of error is prone to biases, the incorporation of errors is sometimes cumbersome and the overall result will be that elements with high uncertainty have low impact on the results. The advantage of option b) is that for elements which are only moderately affected by the correction for AP the approach of incorporating the corrected values in combination with their uncertainty is more "honest" approach for interpreting the results.

Option c) has the disadvantage that elements which might contain information for some - clean - samples, are excluded from the results.

In this thesis options b) and c) are used:

Option c) is used for all elements with very high correction factors. For determining the group of elements which should be skipped due to potentially high bias by adhering particles the results of Figure 6.5 and Figure 6.8 are used.

Figure 6.8 shows that the elements Ti, Th, U, Nb, Zr, Hf and Sc are a group of elements which are similarly affected by the correction for AP. All other elements are differently affected by the correction. Combining the results of Figure 6.5 and Figure 6.8 elements with a generally high correction factor and which are similarly affected by the correction for AP are going to be considered as mainly determined by airborne soil dust. This could also explain findings described in previous publications: For example Matsuura et al. (2001) noted that the elements Fe, Zr and Th have high variance between samples and explained this with inhomogeneity of black tea leaf samples. This could also well be the effect of contamination by APs. In summary the elements Ta, Ti, Th, U, Nb, Zr, Hf and Sc will be excluded in the following, as well for the ionome description as for further statistical analysis.

Option b) is used for all remaining elements. For elements with a very small correction factor, such as the elements of group 3 of the dendrograms (Figure 6.7), original and corrected data are very similar. If a subset of elements is used which consists only in these elements the additional error induced by correction for AP can be neglected while using the statistical tools. If a subset of elements is used containing one element which has a high probability to be notably affected by the correction for AP statistical tools should incorporate these errors, e.g. as weights.

6.4. Summary

Air borne dust on tea leaves can have a major effect on concentrations of some trace elements and the nutrients Fe, Na and Mn. To be able to compare tea data from different regions of climatic conditions, plucking periods, etc. a correction for AP should be calculated. Averages of tea soils of the region or upper crust may serve as an adequate approximation for the elemental composition of the APs in absence of aerial dust data. There are three methods to handle element concentrations after applying the correction for AP:

1. The element concentrations of Ta, Ti, Th, U, Nb, Zr, Hf and Sc will be excluded because they have a high probability to be intensely affected by APs.
2. If a subset of elements is used which contains one of the elements Mo, Tl, Sb, Cs, Pb, Na, Co, Al, Cr, Y, Li, La or Fe ther errors induced by the correction for AP should be incorporated into statistical analysis and interpretations
3. If a subset of elements is used which consists only of elements of S, P, Ca, K, Mn, Cu, Cd, Zn, Sr, Rb, Mg, Ni and Ba the correction for AP can be neglected.

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Figure 6.8.: Heatmap of p-values calculated by paired t-test between distribution of pairwise log-ratio of original tea data versus corrected tea data. P-values of log-ratios of element pairs are colored blueish if they are below 0.05 (alternative hypothesis: true difference in means is not equal to 0) and are colored greenish to yellowish if values are above 0.05 (the means of two populations are equal).

The distribution of log-ratios of Zr~Sc, Ti~Th, Nb~Th, Nb~Hf and U~Hf have the same mean in original and corrected data. That indicates that the correction factor for these elements is always very similar, e.g. if Zr has a high correction factor in one sample, Sc will have a very similar correction factor, and vice versa. The log-ratios of Li~La and Hf~Th have p-values slightly above 0.05 indicating a high probability that the means of the two log-ratio distributions are the same before and after the correction. Additionally the log-ratios Ta~Ti, Ta~Th, Sc~U, Fe~La, Fe~Zr and Hf~Sc have p-values only slightly below 0.05 indicating that the probability for equal means is low but still notable.

For Y all displayed p-values of the t-tests of pairwise log-ratio between original and corrected data have values close to zero, hence the distribution of log-ratios containing one of these elements have different means before and after the correction for AP.

7. Ionome and Elemental Distribution of Tea Leaf

The elemental composition of plucked leaf samples differs by type of tea plant tissue and is additionally influenced by environmental parameters (Chapter 2). The processed tea samples are a melange of tissue types (Section 4.1.1) and are often blended with processed leaves which had been grown in heterogeneous environmental conditions. Hence, the ionome of processed tea samples of a tea garden can be subject to considerable variation despite originating from the same provenance.

The aim of this chapter is to unravel which element subcompositions are suitable for which sample group to serve as possible proxy for the provenance of the tea leaves. This is achieved through the following steps: A) The ionome of plucked leaf samples and processed tea samples are described, compared with published data and discussed. Attention is also paid to within-garden variability. B) The ionomes of the sample groups are compared, namely shoot tips vs. mature leaves and shoot tips vs. processed teas. The results of the first comparison help to assign samples with higher probability into one of the two sample groups or a subsets of a group. The results of the latter comparison help to determine subcompositions of which all element log-ratios are independent of the sample groups or subsets of a sample group.

Tea leaf samples will be described by sets of elements which are divided into macro-nutrients, micro-nutrients, beneficials and non-nutrients (Table D.2). The subcomposition of analyzed macro-nutrients consists of Ca, K, Mg, P and S, the set of analyzed micro-nutrients in Cu, Fe, Mn, Mo, Ni, Zn, and the subcomposition of analyzed beneficial elements in Al, Co, Na and REE (e.g. H. P. Carr et al. 2003; Barker and Pilbeam 2015). All other analyzed elements are considered as non-nutrients. These are Ba, Cd, Cr, Cs, Li, Pb, Rb, Sb, Sc, Sr and Tl. Elements which are strongly influenced by adhering particles (Section 6.4), are excluded from this list.

7.1. Ionome of Shoot Tip

The highest element concentrations are found for the macro-nutrients K, P, Ca, S and Mg (Table 7.1, Figure 7.1). Out of the micro-nutrients the elements Mn, Fe, Zn, Cu and Ni are found in medium concentrations, while Mo is found in minor concentrations. The beneficial elements show medium concentrations for Al and Na and minor concentrations for Co and REE. Out of the non-nutrients the elements Rb, Sr and Ba are found in medium concentrations and all remaining elements, Cr, Cs, Pb, Li, Tl, Cd, Sc and Sb are found in minor concentrations.

Comparing with published data the concentrations of the macro-nutrients are consistent with literature data within the standard deviations (Table 7.1). For the micro-nutrients the concentrations of Mn, Fe, Zn and Cu coincide within one order of magnitude. Among the beneficial elements Al and Na show a magnitude less average concentration than published in previous works. The beneficial elements Co and the REE, on the other hand, are found in comparable concentrations within the standard deviation. Out of the non-nutrients the elements Cr and Cd have the same order of magnitude as published by Y. Chen et al. (2009). For the other micro-nutrients Mo and Ni and the non-nutrients there are no published data for shoot tips yet.

In summary, measured concentrations in shoot tip samples agree generally well with previous published tea leaf data. Al has presumably higher concentrations because the samples of Y. Chen et al. (2009) are considerably older, approximately one month of age, and therefore the Al-accumulating process in leaves had been active longer (Sections 2.1.3 and 7.4.1). The samples of H. P. Carr et al. (2003) have about the same age as shoot tips of this thesis and show comparable concentrations with 381 ± 80 mg/kg. The differences in Na concentrations can not be explained.

The spread of concentrations is calculated by standard deviation of clr values (clr calculated by all elements, Table 7.1). The smallest spread is found for the nutrients and Al. Only the micro-nutrients Ni and Mo show comparably wide scatter of concentrations. For Ni the spread is produced by highly different Ni concentrations between samples originating from Paraná and São Paulo (Figure 7.1). Mo concentrations are highly variable in all listed tea growing areas. All beneficial elements have high spread of data - except for Al which shows a similar spread of concentrations as the nutrients S and P. Al has probably a similar small spread in concentration compared to other nutrients because Al is reaching mature leaves by xylem transport and is further exported to the shoot tips by phloem transport (Tolra et al. 2011). Only a certain proportion of the Al is stored in the

vacuole or cell walls of epidermal cells, similar to e.g. potentially toxic elements. Out of the non-nutrients Sb, Cd, Rb, Sr and Ba show moderate spread of concentrations while all other non-nutrients have high spread, with Cs having the highest (Table 7.1).

Ionome variability with respect to provenance analysis For the main research region Darjeeling a case study was conducted to determine element subcompositions which have a smaller intra-garden variability than the variability between the tea growing areas in Darjeeling. Eight sampling locations at different tea gardens had been sampled three times at spots which form a triangle of approximately 50 m side length. At seven of the sampling location the tea bushes are plants grown from seeds of more than 110 y of age. Only in Makaibari the plant material originates from 30 y old tea plant clones of type 'Dushara'. To compare the ionomes of all 24 shoot tip samples the concentrations had been converted into clr-values by using all elements, including REE but excluding elements influenced by the correction for adhering particles (Section 6).

Figure 7.2 displays the clr-values for all 24 shoot tip samples. For each element the samples originating from the same sampling locations are plotted in same color in one row, so that the dots dodge vertically by garden. If the three dots of one garden are plotting closely, the intra-location variability of the respective element concentration is small, and vice versa. Table 7.2 gives the standard deviation of clr-values for each element for each sampling location as a measure for the spread of clr-values within one sampling location. The average spread (median of the stdev per element) gradually increases in this order: Ca, Al, Y, Ba, Li, K, Sb, Cu, La, S, Rb, Ni, P, Mg, Mo, Mn, Pb, Sr, Zn, Ti, Na, Cr, Fe, Co, Sc, Cd, Cs. Hence, Ca, Y and Al show in general only minor spread of element concentration at one location and the intra-location variability is often smaller than the between-location variability. On the other hand, for elements like Fe, Cs, Sc, Cd or Co the intra-location variability might exceed the spread of data between the locations.

For discriminating between regions the element subcompositions are important which have small intra-location variability but potentially large spread between regions. For example Ba fulfills these conditions: Ba has a average small spread of concentrations within one location (Table 7.2), but the spread for tea samples from various regions is notably bigger (clr-stdev in Table 7.1). Figure 7.2 confirms that Ba has distinguishable average clr-values for certain tea gardens in Darjeeling: Tumsong and Seeyok have the same average Ba-clr-values, Mullootar, Sungma and Tumsong, and Makaibari and Sourennee. For Darjeeling, the element Y has the largest spread of clr-values in ratio

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to average clr-standard deviation of samples from one location (ratio = 3.5). This ratio gradually decreases from Y in this order: Tl, Cs, Pb, Na, Ca, Ni, K, Mn, Co, Sb, La, Rb, Cr, Li, Ba, Mo, P, Fe, Zn, Cu, Mg, S, Sc, Sr, Al and Cd. According to this parameter, in Darjeeling element subcompositions containing the non-nutrients Tl, Cs, Pb, Sb, the beneficial elements REE, Na, Co, and the nutrients Ca, Ni, K and Mn may well serve as proxies for provenance analysis. On the contrary, the elements Cd, Al, Sr, Sc, S, Mg, Cu, Zn, Fe and P have probably less impact for discriminating between regions in Darjeeling.

Figure 7.1.: Ionomes of shoot tip samples ($N = 160$), grouped by tea growing regions. Elements are ordered by median of all samples. Median for each sample group is marked by a colored symbol, the shaded areas mark the second and third quartile. Median values are listed in Table 7.1.

Table 7.1.: Shoot tip concentrations [mg/kg] and clr-values, compilation of data of this thesis (N = 160) and data from Cao et al. (1998) (N = 3), H. P. Carr et al. (2003) (N = 3), Y. Chen et al. (2009) (N = 24) and Jin et al. (2008) (N = 20). The compilation of published data is displayed in the columns left of the marker 'Publ.'. The 'mad' denotes the median absolute deviation of the concentration values and the 'stdev' the standard deviation. The geometric mean for calculating the clr-values is based on all elements listed in this table. Nutrients are marked with an asterisk, beneficial elements with a dagger.

	median	mad	mean	stdev	clr-median	clr-stdev	Publ.:	median	mad	mean	stdev	N
Al [†]	4.9e+02	2.5e+02	6.2e+02	4.1e+02	6.80	0.47		2.4e+03	5.1e+02	2.5e+03	1.1e+03	27
Ba	2.3e+01	1.3e+01	2.4e+01	1.3e+01	3.60	0.64						
Ca*	4.2e+03	1.1e+03	4.3e+03	1.1e+03	8.90	0.40		3.7e+03	1.6e+02	4.3e+03	2.5e+03	30
Cd	1.4e-02	8.6e-03	2.0e-02	1.8e-02	-3.60	0.63		6.0e-02	1.5e-02	5.6e-02	1.8e-02	24
Co [†]	1.4e-01	1.2e-01	2.9e-01	7.7e-01	-1.40	1.10		1.4e-01	3.7e-02	1.7e-01	8.3e-02	24
Cr	5.5e-01	4.5e-01	5.2e-01	3.5e-01	-0.15	0.96		4.6e-01	6.7e-02	5.2e-01	2.1e-01	24
Cs	9.6e-02	8.9e-02	1.6e-01	1.6e-01	-1.80	0.99						
Cu*	1.6e+01	4.1e+00	1.8e+01	1.9e+01	3.40	0.54		1.3e+01	3.8e+00	1.4e+01	4.4e+00	47
Fe*	5.9e+01	1.7e+01	6.4e+01	3.1e+01	4.60	0.56		9.2e+01	1.7e+01	9.1e+01	2.1e+01	27
K*	2.3e+04	3.0e+03	2.3e+04	3.3e+03	11.00	0.42		1.8e+04	2.6e+03	1.8e+04	2.2e+03	27
La [†]	6.3e-02	5.0e-02	1.1e-01	1.7e-01	-2.20	0.64		8.6e-01	5.9e-02	8.8e-01	7.8e-02	3
Li	5.6e-02	3.9e-02	1.0e-01	2.1e-01	-2.30	0.92						
Mg*	2.4e+03	4.7e+02	2.4e+03	4.6e+02	8.40	0.44		2.2e+03	2.1e+02	2.3e+03	5.6e+02	30
Mn*	4.4e+02	2.4e+02	4.8e+02	2.9e+02	6.60	0.65		1.1e+03	1.6e+02	9.5e+02	3.6e+02	30
Mo*	2.5e-02	1.7e-02	3.8e-02	3.7e-02	-3.20	0.94						
Na [†]	2.0e+01	1.5e+01	2.9e+01	2.8e+01	3.50	1.10		1.1e+02	3.0e+01	1.1e+02	2.2e+01	24
Ni*	7.3e+00	4.4e+00	9.0e+00	9.4e+00	2.60	0.84						
P*	4.5e+03	1.1e+03	4.5e+03	1.2e+03	9.00	0.53		2.3e+03	1.3e+03	2.4e+03	9.0e+02	24
Pb	1.7e-01	1.5e-01	2.9e-01	2.8e-01	-0.98	0.78		2.8e+00	5.2e-01	3.3e+00	1.1e+00	24
Rb	4.2e+01	2.6e+01	4.9e+01	3.7e+01	4.20	0.75						
S*	2.8e+03	5.1e+02	2.8e+03	4.6e+02	8.50	0.44		2.8e+03	1.9e+03	2.8e+03	1.2e+03	3
Sb	5.7e-03	2.8e-03	7.0e-03	4.7e-03	-4.50	0.53						
Sc	8.2e-03	6.3e-03	1.1e-02	9.1e-03	-4.10	0.82						
Sr	1.5e+01	8.8e+00	1.6e+01	8.7e+00	3.20	0.62						
Tl	1.2e-02	1.1e-02	2.2e-02	2.6e-02	-3.90	0.97						
Y [†]	9.8e-02	8.5e-02	1.5e-01	1.8e-01	-1.80	0.66		1.5e-01	3.0e-02	1.5e-01	2.0e-02	3
Zn*	3.9e+01	1.2e+01	4.5e+01	2.9e+01	4.30	0.62		2.6e+01	1.9e+00	2.7e+01	4.8e+00	27

Figure 7.2.: Clr-values of shoot tip ionomes of eight sampling location in tea gardens of Darjeeling. Each sampling location consists of three closely located sampling spots, represented by the colored dots ($N=24$). The dots are vertically dodged by garden: For each element the upper row of dots represents Tumsong and the lowest row of dots represents Ging. Clr-values are calculated by all listed elements. Elements are ordered as in Figure 7.1.

Table 7.2.: Standard deviation of clr-values of shoot tip analysis per garden. Clr-values had been calculated by all elements unaffected by correction for adhering particles (Table D.1). 'N' is number of analysis for calculating the standard deviation.

Garden	N	Al	Ba	Ca	Cd	Co	Cr	Cs	Cu	Fe	K	La	Li	Mg	Mn
Ging	3	0.12	0.04	0.05	0.56	0.35	0.20	0.49	0.20	0.21	0.19	0.11	0.06	0.25	0.26
Makaibari	3	0.15	0.10	0.16	0.25	0.33	1.00	0.69	0.25	0.54	0.21	0.17	0.28	0.17	0.15
Mollutar	3	0.09	0.12	0.14	0.52	0.39	0.14	0.39	0.11	0.15	0.10	0.03	0.13	0.22	0.15
Seeyok	3	0.17	0.20	0.01	0.24	0.34	0.32	0.03	0.23	0.35	0.16	0.39	0.36	0.14	0.11
Sourennee	3	0.42	0.16	0.28	0.33	0.15	0.76	0.24	0.30	0.34	0.29	0.66	0.15	0.42	0.46
Sungma	3	0.11	0.10	0.08	0.68	0.26	0.76	0.40	0.14	0.35	0.15	0.14	0.10	0.10	0.29
Tukdah	3	0.12	0.60	0.05	0.15	0.19	0.13	0.20	0.11	0.18	0.11	0.20	0.15	0.26	0.11
Tumsong	3	0.04	0.21	0.14	0.24	0.18	0.24	0.19	0.11	0.19	0.12	0.22	0.21	0.07	0.24

Garden	N	Mo	Na	Ni	P	Pb	Rb	S	Sb	Sc	Sr	Tl	Y	Zn
Ging	3	0.24	0.16	0.35	0.19	0.05	0.18	0.18	0.26	0.05	0.25	0.24	0.13	0.26
Makaibari	3	0.17	0.33	0.17	0.23	0.23	0.31	0.18	0.11	0.39	0.19	0.58	0.31	0.27
Mollutar	3	0.18	0.09	0.21	0.13	0.20	0.17	0.11	0.18	0.14	0.13	0.16	0.03	0.06
Seeyok	3	0.57	0.25	0.29	0.29	0.22	0.18	0.24	0.30	0.42	0.27	0.09	0.07	0.27
Sourennee	3	0.46	0.32	0.20	0.35	0.44	0.13	0.34	0.37	0.13	0.24	0.31	0.22	0.33
Sungma	3	0.13	0.31	0.18	0.18	0.46	0.22	0.14	0.11	0.99	0.19	0.12	0.14	0.24
Tukdah	3	0.20	0.27	0.14	0.20	0.11	0.41	0.12	0.11	0.36	0.53	0.54	0.16	0.23
Tumsong	3	0.23	0.04	0.14	0.12	0.31	0.10	0.14	0.08	0.28	0.10	0.24	0.14	0.20

7.2. Ionome of Mature Leaf

The ionome of the source (mature) leaves differs from the ionome of shoot tips, although the total concentration of analyzed elements is about the same. Compared to sink leaves (shoot tips), they are depleted in elements which are transported via the phloem into the sink tissue. The phloem-immobile elements are higher concentrated in the source leaves compared to the sink leaves. The element Al is significantly enriched in mature leaves, as has been frequently reported in previous publications (Sections 2.1.3 and 7.4.1).

The highest concentrations in mature leaves are found for macro-nutrients and Al (Table 7.3). Out of the micro-nutrients Mn is highly concentrated, Fe, Zn, Cu and Ni are medium concentrated and Mo is found at minor concentrations. The beneficial elements are all found at minor concentrations, except for Na, which is medium concentrated and Al, which is found at concentrations similar to the macro-nutrients. The non-nutrients Ba, Sr and Rb are found at medium concentrations, while all other non-nutrients occur only at minor concentrations. The spread of concentrations is in general higher than calculated for the shoot tip samples. This is probably a result of the very few analysis of mature leaves and therefore will not be further discussed here.

Compared to the data published by H. P. Carr et al. (2003) Al, Ca, Mg and Mn have the same order of magnitude in concentration, while K is found in one order of magnitude less concentration (Table 7.3). Han et al. (2006) describes an increasing accumulation of Pb with progressing leaf development up to 3.5 mg/kg in one year old mature leaves¹. For all remaining elements no data have been published yet.

Regional differences of the ionomes with respect to provenance analysis Figure 7.3 shows that mature leaves sampled in Darjeeling are found in lower concentrations of the macro-nutrients K and P than the other three regions. This pattern can not be seen in for the shoot tips in Figure 7.1. Presumably the lower concentrations in K and P in mature leaves of Darjeeling reflects a lower availability of these two macro-nutrients compared to the other three regions: All mature leaf samples of Darjeeling originate from tea gardens which had farmed without artificial fertilizers for several years, and only relied on self-made compost and dung. The gardens of Brazil and Japan had regularly applied fertilizers which comply with USDA organic standards (USDA organic 2018).

The elements Al, Rb, Sr, Ba, Ni and Cr are found to have higher concentrations in mature leaves from Darjeeling than from the other regions. The high Rb contents could be a reaction of the plant to the low K availability if Rb is replacing K due its similar

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physicochemical characteristics like valence and ion diameter (Tyler 1997; Vinichuk et al. 2010, and references therein). A similar reaction could explain the higher contents of Sr and Ba in Darjeeling mature leaves: If the soils provide a poor availability of the main nutrient Ca the plants might activate ion transporters which are less sensitive to macro-nutrients with respect to their chemically similar elements.

It remains unclear whether the high content in Al is an effect of less fertilizer application. On the one side, poor availability of macro-nutrients might stimulate the plant to release more root exudates of acidic composition. This locally reduces the pH in the rhizosphere and would increase the availability of required nutrients for the plant uptake and, along with it, increase concentration of Al-ions in the soil solution (Section 2.1.2). On the other side, the Al concentration is strongly influenced by the age of the mature leaf (Section 2.1.3) and small differences in the plucking standard during sampling can have a notable impact on the average Al concentration for these small numbers of samples.

The differences in concentration of nutrients and their respective replacement elements between regions is clearly visible for mature leaf samples but not for shoot tip samples. This suggests that mature leaves may 'buffer' the element flux from soils into the shoot tips: The mature leaves, doing actively respiration, receive via the xylem transport the ions from the root-system and export the nutrients and proteins required by the shoots into the phloem tissue. This process obviously seems to favor a stable ratio of the nutrients K, P, S and Mg to C, H, N and O for sink tissue. For provenance analytics a possible 'buffering' by mature leaves implies that a high percentage sink tissue in the analyzed plant material reduces the geochemical signal derived by element uptake from the underlying soils.

Figure 7.3.: Ionomes of mature leaf (N = 27), grouped by tea growing regions. Elements are ordered by median of shoot tip. Median for each sample group is marked by a colored dot, the shaded areas mark the second and third quartile. Median values are listed in Table 7.3.

Table 7.3.: Mature leaf concentrations [mg/kg] and clr-values, compilation of data of this thesis (N = 27) and data from H. P. Carr et al. (2003). The compilation of published data is displayed in the columns left of the marker 'Publ.'. The 'mad' denotes the median absolute deviation of the concentration values and the 'stdev' the standard deviation. The geometric mean for calculating the clr-values is based on all elements listed in this table. Nutrients are marked with an asterisk, beneficial elements with a dagger.

	median	mad	mean	stdev	clr-median	clr-stdev	Publ.:	median	mad	mean	stdev	N
Al [†]	5.5e+03	3.1e+03	5.9e+03	2.5e+03	8.40	0.45		6.9e+03	9.6e+02	6.9e+03	6.4e+02	3
Ba	6.6e+01	4.8e+01	8.2e+01	6.0e+01	4.10	0.59						
Ca*	9.1e+03	2.7e+03	9.6e+03	3.0e+03	8.90	0.44		1.9e+04	4.0e+03	1.9e+04	2.7e+03	3
Cd	1.4e-02	9.5e-03	1.6e-02	8.5e-03	-4.60	0.48						
Co [†]	5.6e-02	2.6e-02	5.0e-02	2.3e-02	-3.40	0.56						
Cr	7.8e-01	4.3e-01	7.4e-01	3.3e-01	-0.61	0.63						
Cs	6.2e-02	5.4e-02	7.9e-02	6.7e-02	-3.00	1.10						
Cu*	7.1e+00	1.6e+00	8.5e+00	4.9e+00	1.60	0.58						
Fe*	1.0e+02	5.5e+01	1.0e+02	5.6e+01	4.10	0.91						
K*	1.2e+04	3.1e+03	1.3e+04	3.2e+03	9.00	0.61		2.9e+03	1.8e+03	2.9e+03	1.2e+03	3
La [†]	4.3e-01	3.3e-01	5.5e-01	5.7e-01	-1.30	0.52						
Li	1.8e-01	1.9e-01	5.9e-01	1.1e+00	-2.10	1.20						
Mg*	1.6e+03	5.7e+02	1.7e+03	6.3e+02	7.10	0.63		2.6e+03	5.1e+02	2.6e+03	3.4e+02	3
Mn*	1.1e+03	9.6e+02	1.4e+03	1.2e+03	6.60	0.78		1.3e+03	2.8e+02	1.3e+03	1.9e+02	3
Mo*	2.4e-02	9.1e-03	3.5e-02	3.0e-02	-4.10	0.84						
Na [†]	1.9e+01	6.8e+00	1.9e+01	7.8e+00	2.50	0.75						
Ni*	4.0e+00	3.3e+00	3.9e+00	2.4e+00	0.88	0.65						
P*	1.7e+03	7.9e+02	1.9e+03	8.7e+02	7.10	0.72						
Pb	5.9e-01	3.7e-01	5.9e-01	2.8e-01	-0.87	0.41						
Rb	2.0e+01	1.1e+01	2.1e+01	1.2e+01	2.60	0.68						
S*	2.4e+03	7.4e+02	2.4e+03	5.4e+02	7.30	0.60						
Sb	1.4e-02	6.3e-03	1.5e-02	7.8e-03	-4.60	0.39						
Sc	3.8e-02	3.3e-02	6.3e-02	5.7e-02	-3.40	0.86						
Sr	3.5e+01	1.6e+01	4.1e+01	2.2e+01	3.40	0.65						
Tl	2.6e-02	1.1e-02	3.7e-02	2.7e-02	-3.70	0.87						
Y [†]	8.8e-01	9.4e-01	1.1e+00	1.0e+00	-0.59	0.75						
Zn*	1.5e+01	2.3e+00	1.7e+01	6.5e+00	2.60	0.54						

7.3. Ionome of Processed Tea

This section describes the ionomes of black tea, green tea, oolong and pu-erh tea, which are produced from shoot tips. Most types of processed teas are produced from shoot tips, harvested with the plucking standard '2 and bud' or '3 and bud'. White tea is in this section excluded because white tea in sensu strictu consists only of tea buds without the second and third leaves and accordingly is not directly comparable to the sampled shoot tip sample. The elemental composition of processed teas may differ from the ionome of plucked leaf samples due to different sink/source leaf ratio and contamination through the processing. The elemental composition of processed tea samples is similar to the averaged ionome of shoot tip samples for subcompositions of elements, which are unaffected by leaf development stage (Section 7.4.1 and Table D.1).

Table 7.4 displays the average concentrations for the analyzed elements in processed tea samples: For all macro-nutrients and most micro-nutrients the values of shoot tips and processed teas are alike. The micro-nutrient Mo is in average higher concentrated in shoot tips and the micro-nutrient Fe is in average higher concentrated in processed teas. Out of the beneficial and non-nutrient elements, the Cr concentration is on average slightly greater in shoot tips while REE, Pb, Sb, Sc, Cs and Tl concentrations are considerably greater on average in processed teas.

The concentrations of the macro-nutrients, micro-nutrients, beneficial elements and non-nutrients are generally very well consistent with published data (Table 7.1, Szymczycha-Madeja et al. (2012) and references therein). Only the elements Fe, Pb, Cr, La, Cd and slightly Li and Na show notably higher concentrations in the compilation of literature data. Fe and La are elements typically influenced by contamination of adhering particles (Figure 6.5). The plant data of this thesis are corrected for adhering particles (Chapter 6) and therefore are expected to show lower concentrations than uncorrected data. Pb and Cr are elements typically influenced by contamination through machine abrasion (Section 7.5.1). Processed tea data of this thesis are mainly derived of whole leaf grades, like TGFOP (Table A.2) and originating mainly of Darjeeling. The sample material at the publications is often described as "tea bags", which are commonly filled with tea leaf grades of smaller particles sizes, like blends of fannings and dust grades. Hence, it can be assumed that these processed tea samples had a higher percentage of the fine particles of machine abrasion which are inherent to finer grained leaf material (Section 2.3.3). Alternatively, the processed tea samples blends analyzed by the other authors contained higher percentage of teas similar to Assam: Figure 7.4 shows that

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Assam has notably higher concentrations e.g. in Pb, Cr and Cu than the Japanese teas of this thesis, which had been produced very delicately and semi-manual. The in overall greater concentrations of Cd, Na and Li can not be explained by one of the parameters discussed in this thesis.

The spread of data is calculated by the standard deviation of the clr-values (Table 7.4). For most nutrient elements the ionomes of processed teas have spread similar to data of the shoot tip samples. Only Fe, Mn, Mo and Ni have differing spread between shoot tips and processed teas. Among the beneficial elements and non-nutrients the elements Cd, Cr, Sc, Tl, Rb, Al, Li show typically a spread of data comparable to shoot tips, while Pb, Sb, Cs, REE, Co, Sr and Na show less comparable spread. Generally, shoot tip samples exhibit a greater spread of concentration than processed tea samples, only Cr, Fe, Pb and Sb show a notably greater spread in processed tea samples. The Cr, Pb and Sb concentrations in processed tea samples display a wide spread which are well consistent with the results of ilr-ANOVA in Section 7.5.1. It is most probable an effect of varying contamination by metal abrasion, either during the manufacturing itself or by airborne dust. The great spread of Fe concentration in processed tea samples could be caused by combined effects of metal abrasion, airborne dust, accumulated either in the field or during the withering process, and lower sink-source leaf ratio of the raw leaf material: all three aspects may contribute to the Fe concentration (Sections 2.3.3, 6.2 and 7.5.1).

Ionome variability with respect to provenance analysis The spread of processed tea data within one garden gives a hint of the variability of processed tea ionomes between years, plucking seasons and plucking sections in the garden. Exemplary, for seven tea gardens with more than three analysis per garden the spread of clr-values is visualized in Figure 7.5 and calculated in Table 7.5. For most gardens the processed tea samples had been derived of one year, only Tumsong was sampled in 2010, 2011, and 2015 and Jun Chiyabari Tea Garden Pvt. Ltd. (Jun Chiyabari) in 2014 and 2015. For all gardens the raw leaf material for the processed tea samples had been derived of different plucking sections, but only for Yamamotoyama do Brasil, São Miguel de Arcaño (S. Miguel de Arcaño) nearly all sections of one division are included into the standard deviation, covering approximately 90 ha of tea plantation. For most elements the spread of clr-values ranges in the same order of magnitude than the spread of clr-values for shoot tips within one sample location (Table 7.2). For the nutrients Co, Cu, Fe, K, Mo, Na, P, S and Zn and the non-nutrients Cr, Pb and Sb the standard deviation is higher

compared to shoot tips of one sample location. Cr, Pb and Sb could be an effect of high fluctuation of contamination of metal abrasion from machines. K, P, S, Co, Cu and Zn show high standard deviation for the two tea gardens Kyoto Obubu Tea Farm, Uji (Obubu) and S. Miguel de Arcaño, the only two gardens in this list which regularly apply fertilizers. For Mo and Na there is no good explanation for high spread of clr-values for some garden, e.g. Tumsong.

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Figure 7.4.: Ionomes of processed tea samples (N = 101), grouped by tea growing regions. Elements are ordered by median of all samples. Median for each sample group is marked by a colored dot, the shaded areas mark the second and third quartile. Median values are listed in Table 7.4.

Table 7.4.: Processed tea concentrations, compilation of data of this thesis (N = 101) and data from Ødegård and Lund (1997) (N = 3), Marcos et al. (1998) (N = 15), Matsuura et al. (2001) (N = 4), Gallaher et al. (2006) (N = 3), McKenzie et al. (2010) (N = 135), Salahinejad and Aflaki (2010) (N = 11) and Seenivasan et al. (2008) (N = 21). The compilation of published data is displayed in the columns left of the marker 'Publ.'. The 'mad' denotes the median absolute deviation of the concentration values and the 'stdev' the standard deviation. The geometric mean for calculating the clr-values is based on all elements listed in this table. Nutrients are marked with an asterisk, beneficial elements with a dagger.

	median	mad	mean	stdev	clr-median	clr-stdev	Publ.:	median	mad	mean	stdev	N
Al [†]	5.4e+02	2.2e+02	6.0e+02	2.9e+02	6.60	0.35		9.2e+02	3.6e+02	1.1e+03	5.5e+02	188
Ba	2.8e+01	1.3e+01	2.8e+01	1.5e+01	3.70	0.61		2.4e+01	1.3e+01	2.5e+01	1.2e+01	177
Ca*	4.0e+03	5.9e+02	4.1e+03	9.0e+02	8.70	0.38		4.6e+03	1.4e+03	4.9e+03	1.7e+03	191
Cd	1.4e-02	7.1e-03	1.9e-02	1.5e-02	-3.90	0.63		9.0e-02	5.9e-02	1.7e-01	2.0e-01	45
Co [†]	1.4e-01	1.0e-01	2.0e-01	1.9e-01	-1.60	0.69		2.1e-01	1.1e-01	2.7e-01	1.4e-01	21
Cr	5.1e-01	4.6e-01	1.8e+00	5.4e+00	-0.41	1.10		2.3e+00	2.0e+00	3.6e+00	5.2e+00	47
Cs	1.3e-01	9.9e-02	1.5e-01	1.1e-01	-1.80	0.94		2.3e-01	1.6e-01	3.4e-01	2.4e-01	19
Cu*	1.6e+01	3.4e+00	1.9e+01	7.2e+00	3.20	0.43		2.0e+01	8.4e+00	2.1e+01	9.6e+00	212
Fe*	7.2e+01	3.7e+01	9.0e+01	7.5e+01	4.70	0.75		1.8e+02	1.1e+02	2.4e+02	1.5e+02	143
K*	2.1e+04	2.1e+03	2.1e+04	2.4e+03	10.00	0.44		1.6e+04	4.3e+03	1.7e+04	4.9e+03	55
La [†]	1.1e-01	7.5e-02	1.5e-01	1.5e-01	-1.80	0.59		8.6e-01	9.1e-01	2.0e+00	2.5e+00	22
Li	6.5e-02	4.2e-02	1.3e-01	2.0e-01	-2.40	0.99		1.6e-01	1.1e-01	1.7e-01	9.3e-02	15
Mg*	2.2e+03	2.9e+02	2.2e+03	3.2e+02	8.10	0.40		2.1e+03	3.6e+02	2.2e+03	4.6e+02	191
Mn*	4.9e+02	2.0e+02	5.3e+02	2.5e+02	6.50	0.38		6.4e+02	3.1e+02	6.0e+02	3.7e+02	191
Mo*	2.4e-02	1.7e-02	4.4e-02	6.8e-02	-3.30	0.76		4.0e-02	1.5e-03	3.8e-02	5.1e-03	4
Na [†]	1.8e+01	1.1e+01	2.2e+01	1.7e+01	3.30	0.89		8.8e+01	6.8e+01	1.6e+02	2.0e+02	114
Ni*	6.8e+00	2.3e+00	7.2e+00	3.2e+00	2.20	0.46		3.8e+00	3.1e+00	4.4e+00	3.5e+00	139
P*	3.9e+03	6.8e+02	4.0e+03	7.2e+02	8.60	0.54		2.9e+03	6.2e+02	3.0e+03	7.0e+02	114
Pb	3.0e-01	1.9e-01	5.0e-01	5.5e-01	-0.79	0.82		9.2e-01	5.3e-01	1.0e+00	6.1e-01	51
Rb	4.8e+01	2.7e+01	5.5e+01	3.5e+01	4.10	0.71		5.3e+01	2.2e+01	5.7e+01	2.2e+01	22
S*	2.6e+03	1.7e+02	2.6e+03	2.4e+02	8.20	0.43		2.5e+03	3.3e+02	2.6e+03	3.8e+02	107
Sb	9.0e-03	6.9e-03	1.3e-02	1.2e-02	-4.20	0.72						
Sc	1.1e-02	8.0e-03	1.7e-02	1.5e-02	-4.10	0.71		5.0e-02	2.2e-02	5.2e-02	1.6e-02	6
Sr	1.6e+01	6.8e+00	1.8e+01	1.2e+01	3.20	0.61		1.7e+01	7.9e+00	1.9e+01	8.3e+00	129
Tl	1.5e-02	1.1e-02	2.2e-02	2.1e-02	-3.90	0.85		5.3e-02	2.4e-02	4.7e-02	1.8e-02	7
Y [†]	1.3e-01	7.5e-02	1.6e-01	1.3e-01	-1.70	0.54		3.6e-01	1.6e-01	3.1e-01	1.3e-01	12
Zn*	3.6e+01	6.3e+00	3.6e+01	7.4e+00	3.90	0.50		2.7e+01	8.1e+00	3.4e+01	6.6e+01	191

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Figure 7.5.: Clr-values of processed tea ionomes of samples from seven gardens of different tea growing regions. The dots are vertically dodged by garden: For each element the upper row of dots represents Tumsonq and the lowest row of dots represents Ging. Clr-values are calculated by all listed elements. Elements are ordered as in Figure 7.1.

Table 7.5.: Standard deviation of clr-values of processed tea analysis per garden. Clr-values had been calculated by all elements unaffected by correction for adhering particles (Table D.1). 'N' is number of analysis for calculating the standard deviation.

Garden	N	Al	Ba	Ca	Cd	Co	Cr	Cs	Cu	Fe	K	La	Li	Mg	Mn
Tumsong	8	0.23	0.21	0.19	0.12	0.36	0.86	0.21	0.17	0.39	0.14	0.34	0.17	0.14	0.29
Sankar	5	0.02	0.15	0.14	0.14	0.04	0.42	0.14	0.14	0.17	0.15	0.14	0.09	0.14	0.17
Ging	4	0.08	0.11	0.09	0.05	0.14	0.13	0.19	0.07	0.10	0.09	0.15	0.32	0.08	0.07
Jun Chiyabari	5	0.10	0.17	0.05	0.34	0.52	0.97	0.43	0.08	0.70	0.11	0.58	0.29	0.12	0.15
Teesta Valley	4	0.13	0.27	0.32	0.08	0.24	0.12	0.06	0.10	0.05	0.23	0.19	0.28	0.22	0.22
Midori-Arcanjo	9	0.31	0.51	0.66	0.63	0.96	0.37	0.51	0.54	0.60	0.58	0.25	0.35	0.51	0.26
Obubu	4	0.70	0.78	0.49	0.10	0.73	0.50	0.80	0.38	0.66	0.32	0.33	0.23	0.23	0.41

Garden	N	Mo	Na	Ni	P	Pb	Rb	S	Sb	Sc	Sr	Tl	Y	Zn
Tumsong	8	0.87	0.71	0.14	0.19	0.30	0.15	0.11	0.45	0.35	0.25	0.09	0.38	0.07
Sankar	5	0.14	0.14	0.14	0.14	0.15	0.15	0.12	0.13	0.62	0.14	0.11	0.05	0.13
Ging	4	0.25	0.14	0.10	0.05	0.10	0.14	0.08	0.32	0.22	0.11	0.24	0.15	0.04
Jun Chiyabari	5	0.65	0.57	0.11	0.10	0.31	0.27	0.04	0.85	0.35	0.17	0.47	0.24	0.07
Teesta Valley	4	0.44	0.19	0.10	0.19	0.11	0.15	0.21	0.08	0.57	0.33	0.22	0.14	0.12
Midori-Arcanjo	9	0.61	0.55	0.35	0.69	0.66	0.24	0.64	0.69	0.61	0.86	0.69	0.78	0.80
Obubu	4	0.46	0.50	0.55	0.44	0.45	0.44	0.28	0.59	0.21	0.45	0.35	0.31	0.52

7.4. Aspects of Shoot Tip/Mature Leaf Ratio in Tea Leaf Samples

The leaf age determines the transition state of the leaves from sink to source leaf (Section 2.1.2). Because the ionomes of sink leaves and source leaves differ considerably for certain elements (Section 7.1 and 7.2) the sink/source leaf ratio, respectively shoot tip/mature leaf ratio influences specific element ratios. For processed tea samples mainly the plucking technique determines the sink/source leaf ratio (Section 2.3.2). To ensure that provenance analytics is independent of the plucking technique or the harvesting method, the analyzed sample set should either contain only samples of similar average leaf age or only subcomposition of elements should be considered where element ratios are unaffected by the leaf development stage. The aim of this section is I) to determine element ratios, which are independent of the leaf development stage and II) to estimate the average leaf age of a tea sample.

7.4.1. Element Distribution between Shoot Tip and Mature Leaf

The distribution of elements between sink and source tissue, i.e. between shoot tips and mature leaves, is described by pairwise log-ratios (Figure 7.6) and clr-vratios (Figure 7.7). The results of comparing the pairwise log-ratio distribution shows which elements are similarly distributed between sink and source leaves. To visualize how the elements are distributed without spurious effects clr-vratios are calculated and displayed in Figure 7.7.

Conclusions from pairwise logarithmic ratios 27 pairs of samples, each pair consisting of one mature leaf sample and one shoot tip sample of the same tea bush, are used for comparing the difference of elemental composition between sink and source leaf tissue. For each sample a matrix of pairwise log-ratios is calculated (Equation 5.1). Then for each element pair the log-ratio distribution of mature leaves is compared with the log-ratio distribution of shoot tips by a paired Wilcoxon signed rank test. The probability-values (p-values) of the result are displayed in Figure 7.6: Greenish to yellowish colored p-values indicate that the mean of the log-ratio distribution of mature leaf samples is equal to the mean of the log-ratio distribution of shoot tip samples, while blueish colored p-values indicate that the means are different. For example, one could interpret that Fe and Cr have similar log-ratios in mature leaves and in shoot tips, but log-ratios of Fe to Ba differ with different leaf development stage.

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Figure 7.6.: Heatmap of p-values calculated by paired Wilcoxon signed rank test with continuity correction between distribution of pairwise log-ratio of shoot tip samples versus mature leaf samples ($N = 27$). P-values of log-ratios of element pairs are colored blueish if they are below 0.05 (alternative hypothesis: true location shift is not equal to 0) and are colored greenish to yellow if values are above 0.05 (the means of two populations are equal).

Figure 7.6 exhibits following relations between mature leaves and shoot tips:

- All log-ratios with Al are different between the two sample groups
- The REE (represented by La and Y) have slightly similar log-ratio distributions between the two sample groups, but are different to all other elements, except for Sc
- The element subcomposition K, Rb, Cs, Cu, Ni, Co, Zn and P have similar log-ratios between the two groups, including Mg~K, Mg~Cu and Mg~Ni, excluding the log-ratios K~Cs, K~Rb, K~Zn, K~P, P~Cu and Cs~Cu.
- All log-ratios with Ba are different between the two sample groups except for Sc

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- All log-ratios with Fe are different between the two sample groups except for Pb, Tl, Mo, Cr and Sb.
- The element subcomposition Na, S and Cd have similar log-ratios between the two groups and additionally there are similar log-ratios for Na~Mo, Na~Mg, S~Mo, Cd~Mo and Cd~Cr.
- The element subcomposition Li, Tl, Sb, Pb, Sr, Mn, Ca and Cr have similar log-ratios between the two groups, except for the log-ratios Mn~Ca, Mn~Sb, Sr~Ca and Sr~Sb. Additionally there is similar log-ratios between Mo~Cr.

The concentration of Al changes with age of the leaves, independent of all other element concentrations. This observation can be very well explained by the Al-accumulating physiological processes of *C. sinensis* (Section 2.1.3). The concentrations of REE also change significantly with respect to all other element concentrations with longer life span of the leaves, but differently than Al. There are two possible explanations for this observation: I) Uptake of Al and La could be correlated in Al-accumulating plants (unpublished data of buckwheat, Sauer and Fahlbusch). II) The correction for adhering particles (Section 6.2) did not fully remove the REE-signal of the AP, and the mature leaves, which are longer time exposed to airborne dust, show therefore higher REE concentrations. This second option would also explain the similar log-ratio distributions of La~Sc (p-value = 0.082), because Sc is also a typical element which is in plants an indicator for APs (Section 6.1.4, Figure 6.2). Probably both options contribute to the REE concentration in mature leaves and therefore the log-ratio distributions are different from shoot tip samples and the log-ratio distribution of Al~La is also different between the two sample groups.

The elements K, Zn and P are typically enriched in sink tissue (Section 2.1.3) because they are phloem-mobile. They play a pivotal role in leaf development. The elements Rb and Cs have roughly similar characteristics as K and accordingly are probably also phloem-mobile. But the p-values of the log-ratios of K~Cs and K~Rb (Figure 7.6) are close to zero, suggesting that the enrichment of K in shoot tips with respect to the mature leaves differs from the enrichment factor of Cs and Rb (see also Figure 7.7). The elements Cu, Ni and Co are micro-nutrients, which are in the same group as the phloem-mobile elements K, Zn and P, indicating that these elements are also enriched in the shoot tips with respect to the mature leaves. In conclusion, the element subcomposition of K, Mg, Cu, Ni, Co, Cs, Rb, Zn and P can be considered as set of phloem-mobile elements, which are enriched in shoot tips with respect to mature leaves.

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The elements Mo, Li, Tl, Sb, Pb, Sr, Mn, Ca, Fe and Cr can be grouped into one subcomposition. This subcomposition does not overlap with elements of the 'phloem-mobile' subcomposition. Because Ca is known to be phloem-immobile, this subcomposition can be considered as phloem-immobile and accordingly is relatively enriched in mature leaves with respect to shoot tips.

The elements Ba, Na, S, Cd and Fe have log-ratio distributions different from those of most other elements. There had no research been conducted yet why these elements in *C. sinensis* have similar log-ratio distributions between mature leaves and shoot tips among each other (except for Ba), but have different distributions with respect to all other elements. Ba, for example, seems to be sensitive to specific soil parameters (unpublished data, Pospiech et al. (2016)).

The two subcompositions of 'phloem-mobile' and 'phloem-immobile' elements have in common that the log-ratio distributions within these element subcompositions are similar between the two sample groups. The grouping of the element subcompositions is also displayed in Figure 6.6 (right plot): The elements of the set K, Mg, Cu, Ni, Co, Cs, Rb, Zn and P are plotting closely suggesting quasi-constant log-ratios between elements. The elements Ca, Sr, Ba, Cd, Tl, Sb, Pb, Mn, Fe and Cr are plotting away from the first element subcomposition as a loose group, with slightly longer links between each other. Al, REE, Sc and Li are plotting as a third set of element, clearly influenced by the mature leaf samples.

Table 7.6 gives the averaged p-values between the log-ratio distributions of mature leaves and shoot tips. The average p-values indicate how probable it is that a log-ratio with this element is comparable between mature leaves and shoot tips:

- Log-ratio distributions with Al and REE (represented by La and Y) have generally very low p-values between the two groups
- Log-ratio distributions with Mg, S, Ba, Cd, Sc, Fe and Na have in average p-values below the threshold of significance of 0.05
- Log-ratio distributions with all other elements have in average p-values above the threshold of significance of 0.05

The results from Figure 7.6 and Table 7.6 lead to the following conclusions:

- Log-ratios with Al, Ba, Sc and the REE are very sensitive to the developmental stage of the leaf

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Table 7.6.: Average of p-values: P-values are calculated by paired Wilcoxon signed rank test between distribution of pairwise log-ratio of shoot tip samples versus mature leaf samples (Figure 7.6). Then p-values of all log-ratios of one element had been averaged. Table is sorted by mean of p-values.

Element	Mean	Median	Var
Al	0.000	3.0e-08	7.9e-07
Y	0.007	3.0e-08	6.3e-04
La	0.011	6.0e-08	1.7e-03
Mg	0.015	1.6e-06	1.6e-03
Mo	0.022	2.3e-05	3.8e-03
Ba	0.027	3.0e-08	2.0e-02
Fe	0.032	1.3e-05	7.8e-03
Sc	0.040	2.3e-05	2.1e-02
Cd	0.054	4.1e-06	2.4e-02
S	0.055	1.5e-07	3.8e-02
Na	0.058	9.5e-05	3.8e-02
Sr	0.062	2.1e-07	4.1e-02
Ca	0.066	6.0e-08	2.4e-02
K	0.072	1.5e-07	4.7e-02
Cu	0.073	3.0e-07	3.5e-02
Sb	0.075	9.8e-07	3.9e-02
Mn	0.079	5.7e-07	5.4e-02
P	0.081	8.9e-08	4.3e-02
Ni	0.089	3.0e-07	4.6e-02
Rb	0.092	3.0e-08	4.9e-02
Li	0.093	2.3e-05	3.8e-02
Co	0.100	7.5e-07	4.0e-02
Pb	0.100	5.2e-05	4.8e-02
Zn	0.100	8.9e-08	5.6e-02
Cs	0.110	6.0e-08	6.8e-02
Tl	0.110	7.5e-06	5.4e-02
Cr	0.130	5.2e-04	5.7e-02

- Log-ratios of elements of the subcomposition Co, Cs, Cu, K, Ni, P, Rb and Zn vs. elements of the subcomposition Ca, Li, Mn, Mo, Pb, Sb, Sr and Tl are sensitive to the developmental stage of the leaf
- Log-ratios with Cd, Cr, Fe, Na, Mg and S are slightly sensitive to the developmental stage of the leaf

Hence, Al, Ba, Sc and the REE should be excluded from element subcompositions for sample groups mixing shoot tip, processed tea and/or mature leaf samples.

Conclusions from clr-vratios Figure 7.7 displays the clr-vratios of the 27 pairs of samples, each pair consisting of one mature leaf sample and one shoot tip sample of the same tea bush. All elements identified in the previous paragraph as primarily phloem-mobile, K, Mg, Cu, Ni, Co, Cs, Rb, Zn and P, are enriched in shoot tips compared to mature leaves. Additionally S, Na and Cd are for most sampled bushes enriched in shoot tips. Most elements identified in the previous paragraph as phloem-immobile, Mo, Li, Tl, Sb, Pb, Sr, Mn, Ca, Fe and Ba, are enriched in mature leaves compared to shoot tips. For Mo, Fe, Sb, Pb and Tl it varies whether the elements are higher concentrated in mature leaves or in shoot tips. Al, Sc and REE are always clearly higher concentrated in mature leaves.

The standard deviation of the clr-vratios is lowest for Ca (0.26), increasing via Mn, Cu, K, S, Al, Cs, Rb, Sb, P, Sr, Mg, Cd, Fe, Y, Mo, Zn, Tl, Ba, Li, La, Na, Pb, Co, Ni, Sc, up to Cr (1.0). A small spread of vratio indicates that for this element the distribution between shoot tips and mature leaves is similar for all sink-source-leaf sample pairs. A large spread of data indicates the contrary. The variability of clr-vratios could either be caused by the plucking technique, plant cultivar or environmental settings. The plucking technique determines the ratio of sink to source leaves (Section 2.3.2) while the pruning technique determines the approximate age of the remaining leaves. Sampling was done carefully according to the plucking standard 'two and bud' (Section 2.3.2) and for mature leaf samples approximately one year old foliage leaves had been chosen. The tea plant samples of Japan originate from different subspecies and cultivars than the tea plant samples from São Paulo or Darjeeling. Additionally, the samples had been harvested at different seasons, which also affects the exact age and developmental stage of the leaf material. That implies that the between regions all three parameters, average development stage of leaves at '2 and bud' plucking standard, plant type and environmental parameters, change at the same time.

There are five sample pairs of identical cultivars, two sample pairs of *Camellia sinensis* var. *sinensis* 'yabukita' (*C. sinensis* 'yabukita') and three sample pair of *Camellia sinensis* var. *sinensis* 'AV2' (*C. sinensis* 'AV2'). The two sample pairs of *C. sinensis* 'yabukita' originate from Uji and in Shizuoka in Japan. The three sample pairs of *C. sinensis* 'AV2' originate all from Makaibari in Darjeeling, India. These five sample pairs are a very small sample group for statistical purposes and results will be statistically uncertain. But the distribution of vratio of this sample group compared to all other sample pairs suggests, that the type of cultivar is not the main source for differences in clr-vratios. For example, for the clr-vratios of Ca the two *C. sinensis* 'yabukita' sample pair clearly plot

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within their respective regional group, while the three sample pairs of *C. sinensis* 'AV2' are spread through the whole group of Darjeeling samples. The third, more probable possibility for differences in the element distribution between source and sink tissue between regions are environmental parameters such as nutrient state of the soils, climate, timing of last pruning, etc. This data set is too small to make assumptions or estimations which of these numerous parameters contribute notably to the differences in the distribution of elements between sink and source leaves.

Figure 7.7 shows that apart from the nutrients P, Zn, Co, Cu, K, Ni, Mg and S the non-nutrients Rb and Cs are enriched in shoot tips compared to mature leaves. The log-ratio analysis (Section 7.4.1 and Figure 7.6) describes that the enrichment factors of Rb, Cs and K are different and Rb and Cs are even higher enriched than the physiochemically similar nutrient K. Ca, Sr and Ba are all enriched in mature leaves compared to shoot tips, with Ba showing the highest enrichment and Ca the lowest. Rb and Cs are both potentially toxic to plants (Gough et al. 1979; Kabata-Pendias 2010). On the other hand as monovalent cations they can serve as substitutes for K, especially on acidic soil, but apparently without replacing K in its metabolic role (Tyler 1997; Kabata-Pendias 2010). There is no explanation yet why during the continuous translocation of ions via the phloem Rb and Cs are preferred over K, while Ca is preferred over Sr and Ba.

In summary, the results of the clr-vratios lead to the following conclusions:

- The distribution of elements is approximately constant for all sample pairs for mainly nutrients, e.g. Ca, Mn, Cu, K, S, P, but also for Al, Rb, Cs, Sb and Sr
- The distribution of elements differs between sample pairs for trace elements, e.g. Cr, Sc, Ni, Co, Pb, Na, REE, Li, etc.
- The type of cultivar does not seem to have an influence on the element distribution patterns.
- Rb and Cs are stronger enriched in sink leaves compared to source leaves than K.

The varying distribution patterns of trace elements could be an effect of the 'buffering' of elements in mature leaves (Section 7.2). In that case, the inhomogeneous distribution of trace elements might veil the geographical fingerprint, especially in the sink leaf tissue. Elements with a constant distribution pattern may serve as proxy for the average age of the leaf tissue (Section 7.4.2).

7.4. Aspects of Shoot Tip/Mature Leaf Ratio in Tea Leaf Samples

Figure 7.7.: Clr-vratios of shoot tip/mature leaf of corresponding pairs of samples (N = 27), grouped by tea growing regions. Elements are ordered by median of clr-vratio. Elements with negative clr-vratios are higher concentrated in mature leaves, elements with positive clr-vratios are enriched in shoot tips.

7.4.2. Estimating the Average Age of Tea Leaf Samples

Figure 7.8.: The value of the balance $[Cu\ K\ |\ Al\ Ca\ Mn]$ vs. the subgroup of samples, further divided by plucking standard and leaf grade. For the shoot tip samples the plucking standard is mostly unspecified, but sampling was similar to the plucking standard '2 and bud'. For black tea all orthodox whole leaf and broken leaf grades containing "fine tippy" and "tippy" are subsumed under 'tippy' (Table A.2). All whole leaf and broken leaf grades containing "golden flowery" and "flowery" are subsumed under 'flowery'. All fannings and dust grades are subsumed under 'dust/fanning'. CTC and green tea leaf grades, which correspond to 'tippy' or 'flowery' leaf grades of the orthodox black tea, had been also subsumed under the respective groups. The plot is based on data collected in this thesis and previously published data (Section 2.1.3, Figure 2.4).

The distribution of elements between source and sink tissue can be used to get a rough estimation of the sink/source leaf ratio of the respective sample. The elements Ca, Mn, Cu, K and Al have the smallest standard deviation of the clr-ratios describing the translocation from source to sink leaves (Section 7.4.1). This suggests that the distribution of these elements between sink and source tissue is less influenced by environmental parameters than other elements. Al and Ca are enriched in source leaves, while Cu, K and Mn are enriched in sink leaves (Figure 7.7). A balanced ratio of these two element sets (Section 5.1, Equation 5.4), noted as $[Cu\ K\ |\ Al\ Ca\ Mn]$, calculates the

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log-ratio contrast between K and Cu to Al, Ca and Mn without spurious effects. The biggest contrast between the two element subcompositions exists for mature leaves and the lowest for shoot tips (Figure 7.8): Mature leaves have an average balanced ratio of -2.7 and shoot tips an averaged balanced ratio of -0.5. Within the group of shoot tips the samples collected with '2 and bud' plucking standard have a smaller log-ratio contrast than samples collected with the '3 and bud' plucking standard; the latter includes one more and further developed leaf. The shoot tip samples marked as 'unspecified' in Figure 7.8 are mostly plucked at '2 and bud' plucking standard, but occasionally with higher percentage of buds. This explains the on average higher balanced ratio value compared to the samples which had been plucked strictly '2 and bud'.

Black, green, oolong and pu-erh tea are all produced from different leaf grades. For the data of pu-erh (McKenzie et al. 2010) and oolong (Herrador and González 2001; McKenzie et al. 2010, and this study) no further specification of leaf grades was available. The authors of Wong et al. (1998) compared oolong, which was produced from tea flushes harvested at '3 and bud' to '4 and bud' plucking standard, with other types of processed tea produced from '2 and bud' plucking standard and proposed to use Al as an age indicator. Black and green teas exhibit different means of [Cu K | Al Ca Mn] values by leaf grades. For black and green teas the leaf grades of 'whole leaf' and 'broken' had been unified into 'tippy' if leaf grade description indicated a high percentage of buds and unified into 'flowery', if description indicated a small percentage of buds. The fine grained leaf grades 'fanning' and 'dust' had been subsumed under 'dust/fanning' (see caption Figure 7.8). It can be seen that processed tea with leaf grades corresponding to "fine tippy" or "tippy" (Table A.2) have a notable higher values for the [Cu K | Al Ca Mn] balance than processed teas of leaf grades corresponding to "golden flowery" or "flowery". The highest leaf qualities for orthodox black teas from Darjeeling, e.g. SFTGFOP or FTGFOP-1, have the highest balanced ratio with a median value ($N = 12$) of -0.25. This clearly reflects a very highest percentage of immature leaves and buds and accordingly a high sink/source leaf ratio.

It has to be noted that the six samples of leaf grade 'dust/fannings' have also a very high [Cu K | Al Ca Mn] balance. The trend of a small log-ratio contrast between K and Cu against Al, Ca and Mn for the fine leaf grades could be confirmed by four processed tea samples of Tumsong sampled during sorting. All four samples originate from the same withering table batch and had been sampled within 10 min at one sorting machine (Figure 7.9) to ensure that the raw processed tea is comparable in its elemental composition. The finest grained sample contained a very high percentage of trichomes, visible

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Figure 7.9.: Sorting machine with 10 sieves for black tea (orthodox) production in Darjeeling. The sieve with the coarsest mesh is on the top (No.8), the sieve with the finest mesh is on the bottom (No.18). For Sieve No.8 the balance is
[Cu K | Al Ca Mn] = -0.82

Figure 7.10.: Detail of Figure 7.9: Output of sieve No.18. The tea hairs are enriched in this leaf grade and accumulated as the beige band on the metal outlet splint.
[Cu K | Al Ca Mn] = -0.52

in Figure 7.10 as yellowish band, and has a [Cu K | Al Ca Mn] value of -0.52. The other three samples, from fine to coarse, are derived from sieve Nr.14 (Figure 7.11), Nr.10 (Figure 7.12) and Nr.8 (Figure 7.9). Their [Cu K | Al Ca Mn] values are -0.68, -0.74 and -0.82, respectively. The last value corresponds very well to the log-ratio contrast between Cu and K to Al, Ca and Mn of the 'flowery' leaf grades of black teas (Figure 7.8).

There are two possible sources of high Cu and K in relation to Al, Ca and Mn in the fine grained leaf grades: I) The abundant trichomes of the leaves, which for tea of high quality plucking standards can make up a significant portion in dust and fanning grades. II) Young leaves and buds have a more delicate tissue which breaks easier under the mechanical stress of production and therefore 'young' tissue is enriched in the finer grained leaf grades. This preliminary study of [Cu K | Al Ca Mn] balance in dependence of leaf grade do not explain why there is a shift in the [Cu K | Al Ca Mn] values by leaf grade. Ajay Kichlu (Chamong Tea Exports Pvt. Ltd.) confirmed that broken and fanning leaf grades contain higher percentages of small leaves and shoot tips than the whole leaf grades, which can also be tasted by experienced tea sommeliers. In summary, not only the plucking standard but also the leaf grade influences the average development stage of leaf particles in a processed tea sample.

This approximation of average developmental stage of the leaf material of the samples can be used to filter sample sets for a specific range of [Cu K | Al Ca Mn] values: The

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Figure 7.11.: Detail of Figure 7.9: Output of sieve No. 14.
[Cu K | Al Ca Mn] = -0.68

Figure 7.12.: Detail of Figure 7.9: Output of sieve No. 10.
[Cu K | Al Ca Mn] = -0.74

higher the minimum [Cu K | Al Ca Mn] values are the higher is the probability that the sample set contains only sink tissue samples, e.g. if the filter is set to [Cu K | Al Ca Mn] > -1 . On the other hand if the filter is set to [Cu K | Al Ca Mn] < -2 the probability is very high, that the sample set consists only of mature leaves.

This filtering can be used for three objectives: I) For statistical analysis where one sample group should consist strictly of sink tissue, II) to decide about the element sub-composition used for analysis, e.g. should elements being sensitive to the developmental stage of the leaves be included or not and III) estimating for processed tea samples the plucking standard as proxy for provenance analysis. For the latter the influence of the leaf grade on the [Cu K | Al Ca Mn] values has to be taken into account.

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In contrast to plucked leaf samples, the sampling location of which can be documented by meter-scale, processed teas are often an average of garden section, and often the exact plucking section of the respective production batch is unknown. Additionally, batches of tea are often blended with other batches, and the resulting lots could even consist of tea material from the whole garden area. Moreover, abrasion of the machinery during the tea processing is an other possible source of contamination (Section 2.3.3) affecting certain element ratios. Every type of processed tea requires its own set of machines and accordingly green tea will have different sources of abrasion than black orthodox tea or black CTC. For provenance analysis of the ready-made product 'tea' the shift in elemen-

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tal composition between plucked leaves and processed teas has to be characterized. This section discusses in detail differences between the sample group of plucked leaves and processed teas.

7.5.1. Effects of Black Tea Manufacturing

This section focuses on metal abrasion sources for black orthodox and black CTC tea by comprising all samples of the subgroups 'black' and 'shoot tip': 74 processed tea samples and 160 shoot tip samples are used as unpaired data set for the analysis. Three methods are used to determine the elements which have a high probability to be altered by machinery abrasion: I) A covariance biplot of clr-transformed data, II) the Mann-Whitney test on distribution of pairwise log-ratios, similar to the method used in Section 7.4.1, and III) an ilr-ANOVA.

I) In Figure 6.6 (right plot) the sample dots of black teas concentrate in the upper left quadrant while the sample dots of green tea are mainly found in the lower right quadrant. On the one hand, the position of the element labels Pb, Zr, Cr and Sb indicate that the log-ratio of one of these elements to one of the other elements is probably in average higher for samples projected into the upper left quadrant. This observation excludes log-ratios with Nb, Ti and U, On the other hand, samples projected into the opposite quadrant, the lower right quadrant, have probably the lowest log-ratios with Pb, Zr, Cr and Sb. This suggests that the concentrations of the elements Pb, Cr and Sb vary between black processed tea samples and green processed tea samples or shoot tip samples. The averaged concentrations of these elements confirm that black tea samples show notably higher concentrations compared to the majority of shoot tip samples and green tea samples (Table 7.7).

Table 7.7.: Averaged (median) element concentration [mg/kg] of Cr, Pb, Sb and Zr by type of processed tea and shoot tip. Table is ordered by median concentration of Pb. 'N' denotes the number of analysis. In this data set exist for oolong and gunpowder only one sample each, but values coincides with published data (McKenzie et al. 2010; Szymczycha-Madeja et al. 2012).

Subgroup	N	Pb	Cr	Sb	Zr
green	26	0.133	0.198	0.005	0.052
shoot tip	160	0.170	0.546	0.006	0.039
oolong	1	0.207	0.377	0.004	0.010
black	74	0.375	0.661	0.011	0.081
gunpowder	1	1.602	0.516	0.051	0.408

II) The Mann-Whitney test is used to calculate the p-values if the means of the pairwise log-ratio distribution between the two sample groups are equal (Figure 7.13). The figure clearly shows that Pb and Sb have similar log-ratio distributions in both sample groups, but differing log-ratio distributions with all other elements. The p-values of all other log-ratio distributions do not permit a clear grouping of elements, but the two main element subcompositions, Mo, Na, Mg, K, S, Ni, Co, Cd, Zn and Ba, REE, Sc, Li, Ti, Sr, Ca, Rb, Al, Cs, Cr, Mn, Fe, Cu, are roughly corresponding to the phloem-mobile/phloem-immobile element subcompositions (Section 7.4.1).

Figure 7.13.: Heatmap of p-values calculated by (unpaired) Mann-Whitney test between distribution of pairwise log-ratio of shoot tip samples (N = 160) versus black processed tea samples (N = 74). P-values of log-ratios of element pairs are colored blueish if they are below 0.05 (alternative hypothesis: true difference in means is not equal to 0) and are colored greenish to yellow if values are above 0.05 (the means of two populations are equal).

III) The ilr-ANOVA of two sample groups shows that Pb, Sb and Cr build one element subcomposition. This subcomposition has the highest variance between the two sample groups black tea and shoot tips (Figure 7.14). Most nutrients are part of the

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element subcomposition of Mo, Co, P, Zn, Ca, Cs, Fe, Mg, K, and Ni. The third element subcomposition consists of Sc, Sr, Mn, Cu, Rb, Li and Tl, whereof Sc builds an own subcomposition. Summarizing the results of the three methods the concentrations of

Figure 7.14.: Graph of ilr-ANOVA (CoDa dendrogram) of shoot tip samples (N = 159) and black processed teas (N = 74) as categorical variable to explore which element subcompositions have a similar behavior with respect to the two sample groups. For calculating the ilr-ANOVA the element subcomposition was used which excludes elements with high probability to be altered by leaf development stage (Table D.1, unaffected element subcomposition of the parameter 'leaf development stage').

Cr, Pb and Sb are clearly altered in black processed tea compared to shoot tips. The concentrations of Sc have a less probability to be significantly altered but the methods of covariance biplots and ilr-ANOVA suggest to include this element to set of elements which could be potential biased by black tea manufacturing.

The source of Pb and Sb is probably lead containing solders. A very frequently used solder alloy consists of Pb and Sn with varying minor contents in Fe, Sb, Cu and Ni (Council of the European Union 2011b). Analysis of Sn does generally not meet the quality criteria to be used for provenance analysis (Section 4.3.1, Table 4.3). But if Sn is included for the ilr-ANOVA, the grouping of Sn with Pb and Sb (Figure D.1, upper graph) supports the assumption that abrasion of solder is the major source of Pb and Sb in processed teas. There are two possible sources of solder abrasion: a) The machinery in the tea factories: Lead containing solders are now restricted by several legislations, e.g. in the EU (Council of the European Union 2011b) and Japan, but for most tea producing areas lead containing solders are still commonly utilized for building or maintaining tea factories. b) Airborne dust: Darjeeling is very close to the cities of Siliguri and Bagdogra

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(Section 3.1.1), both home to thriving industry with a high rate of combustion residues in the air. Other tea growing areas, like Nilgiris, Registro or Shizuoka, are also exposed to airborne dust of industry and road traffic. During the hours of withering the wilted leaves of the tea could act as an air filter (Section 2.3.3) retaining also the particles of solders from industries located in the proximity of the tea growing areas.

One source of Cr is likely to be the metal abrasion of the machines, especially CTC production is prone to (too) high Cr abrasion during cutting and tearing the leaves due to affected teeth of the steel rollers (Section 2.3.3). A study of ~800 Chinese processed tea samples (Han et al. 2005) reveals that Cr in black tea samples (N = 148) are found in significantly higher concentrations, median = 1.73 mg/kg, than green tea (N = 537), median = 0.48 mg/kg, or oolong tea (N = 81), median = 0.27 mg/kg. Because black tea production requires more invasive machinery than oolong or green tea, this study confirms that black tea manufacturing processes are one possible source of Cr in black teas. In the data set used for this thesis the effect of machinery on Cr concentration can not be seen as clearly because the majority of black tea samples are Darjeeling orthodox black teas. The manufacturing procedure used for orthodox black teas, similar to the one used for oolong, does not involve machinery as rough or invasive as used for CTC black tea production. In Figure 7.15 (left plot) the projection of sample dots onto the variable rays indicates, that the clr-vratio of Cr is induced mainly by the samples from Matigara Tea Estate (Matigara) and Ord Terai Tea Garden (Ord Terai). In 2011, both gardens used the oldest CTC machinery of all visited factories; it can be presumed that this caused higher abrasion rates than the other CTC factories in the Maud and Amaya.

Sources of Sc could be a) metal abrasion of Al-Sc-alloys, b) airborne dust during withering - the same effect as described for Pb and Sb -, or c) the accumulation of Sc in mature leaf sample during their life span combined with the fact that the ratio of sink to source leaves is lower in processed teas than in the shoot tip samples. The latter option is supported by the observation that the Sc concentration is slightly sensitive to the leaf development stage (Figure 6.6 and Section 7.4.1). On the other hand, the effect of the leaf age is estimated to be too small to account for an effect of differences in the sink-source leaf ratio between processed teas and shoot tips on the Sc concentration. Additionally the ilr-ANOVA including Al - a strong indicator for leaf age - shows no grouping with Sc, but with Mn (Figure D.1, lower graph). Therefore, it is likely that the Sc concentration in processed teas is due to a combination of all three effects: metal abrasion, airborne dust and ratio of sink leaves to source leaves.

7.5.2. Comparability of Shoot Tips and Processed Teas within a Garden

To assess if there is a compositional shift between shoot tips and processed teas within a tea garden, 53 sample pairs of processed tea and the corresponding shoot tips have been calculated: For processed tea samples with known origin of sections or divisions of the tea garden, the average ionome of all shoot tip samples of the respective section was calculated. For processed tea samples of unknown section or division but known plucking period, the average ionome of all shoot tip samples of the respective plucking period of this garden was calculated. If for processed tea samples only the garden was known as origin, the average ionome of all shoot tip samples of the respective garden was calculated. For each sample pair of processed tea and corresponding average, ionome of shoot tips *vratios* and pairwise log-ratios were calculated. For calculation of the *clr-vratios* all elements were included (Table D.1).

Figure 7.15 displays in the left plot the results of PCA of *clr-vratios* with all elements (Table D.1), the REEs represented by La and Y. The biplot is dominated by the spread of *clr-vratio* values for Cr. The projection of two sample pairs, one of 0rd Terai and one of Matigara, close to the label of Cr, suggests that for these two sample pairs the ratio for Cr of processed tea versus shoot tip is relatively higher than for most other samples and elements. Both tea estates produce mainly CTC black tea. This coincides very well with the results of the previous section that Cr is a typical contaminant through metal abrasion in CTC black tea production (Section 7.5.1). A third sample pair of green tea (matcha) vs. shoot tips from the tea garden 0bubu, which also plots relatively close to Cr, was slightly contaminated by Cr by an unknown source: For the sencha samples of 0bubu Cr is found in a median concentration of 0.10 mg/kg, the bancha sample shows a Cr concentration of 0.13 mg/kg, and the matcha sample shows a Cr concentration of 0.52 mg/kg. Sencha and bancha production in Japan generally excludes machinery which is prone to high metal abrasion. For the matcha sample the production step of pulverization may include machines which are the source of Cr. Element concentrations of Sc, Pb and Sb, which are typically altered through tea production (Section 7.5.1), do not seem to be significantly altered in processed teas compared to shoot tips for the samples of this data subset.

To visualize differences in element ratios of processed tea samples compared to the corresponding shoot tips other than by contamination through the typical machine abrasion, the right plot of Figure 7.15 displays the results of PCA of *clr-vratios* of all elements without the elements Sc, Sb, Pb, Cr and the two nutrients S and P. These two nutrients had been omitted for better visibility of the other labels in the plot, because since they

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Figure 7.15.: Biplots of clr-vratios of processed teas to corresponding ionome averages of shoot tip ($N = 53$). For calculation of the clr-vratios all elements are included (Table D.1). The left biplot displays all elements, REEs represented by La and Y. The right biplot excludes elements affected mainly by black tea manufacturing (Table D.1) and S and P for better visibility. Abbreviations for tea gardens: Amay: Amaya, Md-A: S. Miguel de Arcaño, Maud: Maud, Obub: Obubu, Mrch: Moriuchi, Mkbr: Makaibari, Tmsn: Tumsong, TstV: Teesta Valley, Cstl: Castleton, Dhaj: Dhajea, Jngp: Jungpana, Mryb: Marybong, Ging: Ging, MrgH: Margeret's Hope, Mtgr: Matigara, SImH: Selim Hill, Ord: Ord Terai, Ngrf: Nagri Farm, ShrD: Shree Dwarika, Tkdh: Tukdah.

are macro-nutrients, their concentrations are not influenced by a production step after plucking. The biplot indicates that ratio of Co and the REE between processed tea and shoot tip have a larger variance than the other element vratio. This Co variance seems to be induced mainly by the samples of Teesta Valley. The source of a possible alteration of Co concentration between shoot tips and processed teas in Teesta Valley remains unknown. The REE variance seems to be influenced by several samples of Matigara and S. Miguel de Arcaño. The source of the variance in REE could be incomplete removal of the signature of adhering particles (Section 6.2).

To show which element ratios systematically differ between the processed tea samples and shoot tip samples the distribution of pairwise log-ratios between sample pairs of the

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Figure 7.16.: Heatmap of p-values calculated by paired Wilcoxon signed rank test with continuity correction between distribution of pairwise log-ratio of shoot tip samples versus processed tea samples (sample pairs: $N = 53$). P-values of log-ratios of element pairs are colored if they are below 0.05 (alternative hypothesis: true location shift is not equal to 0) and are colored greenish to yellow if values are above 0.05 (the means of two populations are equal).

two sample groups are compared by a paired Wilcoxon signed rank test (Figure 7.16). The p-values of this test reveal that only few element log-ratios have a location shift not equal to 0, respectively differ between processed teas and shoot tips. These are several log-ratios with Fe, Cu and La, followed by Cd, Cs, Li and Rb (sorted by average p-value). Of these elements, Fe and Cu display the biggest offset in their log-ratios between the two sample groups.

The vratio representation 'alr' with the reference element Fe (Section 5.2) puts the focus on differences of element ratios with Fe between shoot tip samples and the corresponding processed tea samples. The 'alr Fe' is visualized as biplot in the left plot of Figure 7.17: the plot reveals that especially processed tea samples of Selim Hill,

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Figure 7.17.: Biplots of alr-vratios of processed teas to corresponding ionome averages of shoot tip (N = 53). The displayed alr-vratios excludes elements affected by tea manufacturing Sb, Pb, Cr, Sc (Table D.1) and S and P. In the left biplot the reference element for the alr-vratios is Fe, for the right plot the reference element is Cu. Abbreviations for tea gardens are listed in Figure 7.15

Matigara, Teesta Valley and Ord Terai show higher Fe concentrations relative to their corresponding shoot tip samples compared to most other sample pairs. A higher Fe concentration in processed tea samples could be on the one hand, similarly to the REEs, caused by too weak correction for AP or, on the other hand, be caused by contamination through metal abrasion of machinery. Based on the findings of the previous biplots in Figure 7.15, the Fe signal is probably mainly caused by incomplete mathematical removal of APs.

The left biplot in Figure 7.17 displays the PCA calculated on basis of the vratio representation 'alr' with the reference element Cu. The projection of the sample dots onto the PC1/PC2 plane suggests that processed teas of the tea gardens Tumsong, Maud, Tukdah, Marybong and some of Amaya Cu is found in slightly higher concentrations than shoot tips of the respective gardens. In contrast, processed tea samples from Dhajea seem to be considerably less concentrated in Cu in ratio to shoot tips compared to all other gardens. A possible source of Cu could be rolling tables during the step of disruption/rolling (Section 2.3.3). The factories of Tumsong, Tukdah and Marybong both

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have mainly old (>40 y) gun metal rolling tables and only few steel rollers. For Maud and Amaya the types of rolling table is unknown, but the tea makers of Amaya eventually add traces of Cu to their processed tea products. The tea factory of Dhajea has rolling tables made of modern brass metal alloys, installed in 2001. The results indicate that teas rolled on rolling tables made of old brass metal alloys may be slightly contaminated by Cu, while teas rolled on rolling tables of modern brass alloys, or recently installed rolling tables, respectively, or rolled on rolling tables made of steel alloys, have no or only a minor contamination of Cu.

These results do only partly confirm previous works, where for Al, Cr, Cu, Pb and Zn elevated levels had been reported for processed tea (Wong et al. 1998; Fung 2003; Ashraf and Mian 2008; Jin et al. 2008; Seenivasan et al. 2008; Salahinejad and Aflaki 2010, Section 2.1.3). In the data set of this thesis no indication for elevated levels of Al and Zn in processed teas could be statistically ascertained and Cu concentrations are elevated only in very specific samples. Elevated levels of Al could be an effect of the sink/source leaf ratio in the two groups of samples: If the processed tea samples had on average higher contents of mature leaves than the shoot tip samples with which they were compared, i.e. if the processed teas had a smaller sink/source leaf ratio, then Al concentrations could be slightly higher than in shoot tip samples (Section 7.4.1). Elevated levels of Zn could only be explained by a strong contamination of unclear source, because Zn, being a micro-nutrient, is already rather high concentrated in the leaves (Section 7.1, Table 7.1). The results of a statistical approach for all shoot tip samples and black processed tea samples do not confirm on a general basis machine abrasion as possible source of contamination for the elements Al, Cu and Zn. Hence, these elements are not included into the element subcomposition that was possibly altered during tea manufacturing (Table D.1).

7.6. Summary

The measured concentrations in shoot tip, mature leaf and processed tea samples generally agree well with previously published data. For all macro-nutrients and most micro-nutrients the values of shoot tips and processed teas are similar. The smallest spread of data is found for the nutrients and Al.

Mature leaves of Darjeeling show lower concentrations for the macro-nutrients K and P than the other three regions. This probably reflects a lower availability of these two macro-nutrients compared to the other three regions due to the organic soil management

in Darjeeling. Moreover, for mature leaf samples there are clearly visible differences in concentration of nutrients and their respective replacement elements between regions. These differences are not visible for shoot tip samples, suggesting that mature leaves 'buffer' the element flux from soils into the shoot tips. This process seems to favor a constant ratio of the nutrients K, P, S and Mg to C, H, N and O for sink tissue. For provenance analytics the possible 'buffering' by mature leaves implies that a high percentage of sink tissue in the analyzed plant material reduces the geochemical signal derived by element uptake from the soils.

The comparison between intra-location variability versus inter-location variability of element concentrations shows that in Darjeeling the element subcompositions containing Ti, Cs, Pb, Sb, REE, Na, Co, Ca, Ni, K and Mn can serve as proxies for provenance analysis. On the contrary, the elements Cd, Al, Sr, Sc, S, Mg, Cu, Zn, Fe and P have probably less impact for discriminating between regions in Darjeeling.

The distribution of elements between source and sink leaves is as follows:

- The distribution of elements is approximately constant for the nutrients, e.g. Ca, Mn, Cu, K, S, P, and Al, Rb, Cs, Sb and Sr.
- The distribution of elements varies for trace elements, e.g. Cr, Sc, Ni, Co, Pb, Na, REE, Li, etc.
- The type of cultivar does not seem to have an influence on the distribution patterns.
- Rb and Cs are stronger enriched in sink leaves compared to source leaves than K.

The variations of distribution patterns of trace elements could be an effect of the 'buffering' of elements in mature leaves (Section 7.2): This inhomogeneous distribution of trace elements might veil the geographical fingerprint, especially in the sink leaf tissue. Elements with a less variable distribution pattern can serve as proxy for the average age of the leaf tissue.

- Log-ratios with Al, Ba, Sc and the REE are very sensitive to the developmental stage of the leaf.
- Log-ratios of elements of the subcomposition Co, Cs, Cu, K, Ni, P, Rb and Zn vs. elements of the subcomposition Ca, Li, Mn, Mo, Pb, Sb, Sr and Ti are sensitive to the developmental stage of the leaf.
- Log-ratios with Cd, Cr, Fe, Na, Mg and S are slightly sensitive to the developmental stage of the leaf.

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Hence, if shoot tip samples are grouped together with processed tea samples and/or mature leaf samples, the used element subcomposition should always exclude the elements Al, Ba, Sc and the REE.

A balanced ratio of elements which are very sensitive to the developmental stage of the leaf and have a less variable sink/source leaf distribution can help to estimate the average leaf age of a tea sample. In this thesis the balanced log-ratio contrast between K and Cu to Al, Ca and Mn is used, noted as [Cu K | Al Ca Mn]. Mature leaves have an average balanced ratio of -2.7 and shoot tips an averaged balanced ratio of -0.5. This trend is also visible for orthodox black teas from Darjeeling, e.g. the highest leaf qualities have the highest balanced ratio with a median value ($N = 12$) of -0.25. This clearly reflects a high percentage of immature leaves and buds, i.e. a high sink/source leaf ratio, in processed teas of high quality.

The fine grained leaf grades of processed tea samples have also notably high Cu and K in relation to Al, Ca and Mn. There are two possible reasons: I) The abundant trichomes of the leaves, which can make up a significant portion in dust and fanning grades of high quality teas. II) Young leaves and buds have a more delicate tissue which breaks easier under the mechanical stress of production and therefore 'young' tissue is enriched in the finer grained leaf grades. In summary, not only the plucking standard but also the leaf grade influences the [Cu K | Al Ca Mn] ratio.

The values of this balanced ratio can be used to filter samples in order to make sample groups more homogeneous. This is important I) for statistical analysis for known sink/source leaf ratio, II) to compose the element subcomposition used for analysis, e.g. if elements which are sensitive to the leaf development stage should be included or not and III) estimating the plucking standard as proxy for provenance analysis for processed tea samples. For the latter the influence of the leaf grade on the [Cu K | Al Ca Mn] values has to be taken into account.

Processed tea samples, especially black teas, are prone to contamination of Fe and heavy metals. The source of Pb and Sb is probably lead containing solders. One source of Cr is likely to be the metal abrasion of the machines. The source of Sc is probably a combination of metal abrasion of Al-Sc-alloys, airborne dust, accumulation in the field or accumulation during the withering process. The same possible sources apply for Fe. Additionally, different plucking standards could cause the large spread of Fe concentration in processed tea samples by varying sink/source leaf ratios of the leaf material.

8. Influence of Soil on the Tea Ionome

Element uptake by plants is since decades a major research topic. The nutrient uptake by *C. sinensis* had been intensely studied, too, in order to optimize tea cultivation for commercial purposes. But for provenance analysis it is less important why or how elements are transferred into the plant, but rather which element ratios remain constant during the uptake. Aggravatingly, the geochemical composition of tea soils and the bio-availability of elements is subject to seasonal and yearly changes due to measures of soil management. Accordingly, there are a) element ratios influenced by the soil management and b) element ratios which are independent of soil management. The aim of this chapter is to distinguish element subcompositions which are suitable for provenance analysis because they reflect the geochemical composition of the soils and are stable in respect to measures of soil management. The second conditions includes that certain soil management is often subject to the soil type of specific tea growing regions: Eventually, subcompositions of elements influenced by soil management can also serve as a proxy for tea growing regions.

8.1. Soil

Tea soils, and especially the rhizosphere of tea plants, is a very complex and still poorly understood environment. To use the soil data for refining provenance analytics a radical simplification is applied on the soils, deliberately excluding soil parameters like type of soil, pH, etc. The tea soils are characterized solely as an element reservoir for the tea plants and the description therefore focuses only on the geochemical composition. Because the pH of the tea soils is between 3.9–4.5 (Section 2.2, Pospiech 2012) it can be assumed that a high percentage of the total element concentration in soils is potentially available to the tea plant.

As described in Section 4.1.1, topsoil samples are a melange of soil of the upper 15–25 cm and subsoil samples are a melange from below topsoil down to 30–45 cm. Several element concentrations can be subject of strong fluctuation due to longterm,

recent or changing agricultural measures, such as fertilizer applications, remnants of fungicides, application of carbonate/dolomite, plowing in tea litter, etc. (Section 2.2). The geochemistry of topsoils is supposedly stronger affected by these measures than the geochemistry of subsoils. Hence, subsoils have supposedly less variability between years and represent better the geochemical composition of the total soil volume underneath the plant. The contrast between topsoil and subsoil gives an indication of which elements are affected by agricultural measures. These elements are less sound for provenance analysis on tea. In the following sections the subsoil composition is taken as reference.

8.1.1. Geochemical Composition of Subsoils

Figure 8.1 and Table 8.2 give the geochemical composition of all subsoils. The elements Al, Fe, P and Sc are found in approximately the same concentration in all subsoil samples, independent of the region. The elements Zn, Cr, Pb and Cd show minor variations between the regions. All remaining elements are differently concentrated between the regions, whereof the biggest contrast exists between India and Brazil. The biggest contrast between regions in terms of concentration have S, Cs, Ca, Na, Sr, Rb, and K. Except for S, for these elements Brazilian soils are found in lower concentrations than the Indian soils.

Table 8.1) displays the sum of the concentration of nutrient elements. The element Fe is excluded from this sum because it is an abundant element in tropical soils but *C. sinensis* requires it in minor quantities. The Brazilian soils show lower concentration of nutrients than the soils from Darjeeling and Assam in India. Lowest concentration of nutrients is found in Registro, Brazil, with only 0.2 wt%, followed by the soils in São Miguel de Arcanjo with 0.4 wt% and 0.6 wt% and Araucária with in average 0.7 wt%. In Darjeeling and Assam the average concentration of nutrients is approximately three to four times as high. The highest average of nutrient concentration is found in the sampled gardens close to the city Dibrugarh in Assam with 4.3 wt%. The total organic carbon had not been determined, but is in tea soils approximately between 5%–15% (Wang et al. 2010; Karak et al. 2011, 2015b; Li et al. 2016).

Compared to the upper continental crust (Rudnick and Gao 2003) (Figure D.2) the soils are only in S significantly enriched. They are all depleted in the macro-nutrients Ca, Mg and K as well as in the elements Ba, Cd, Na, Sr and Tl. Except for Darjeeling the soils are also depleted in the macro-nutrient P. Other elements which are depleted in the soils of Brazil, but not in all soils of India are Cs, Cr, Mn, P, Co and Sc.

Table 8.1.: Sum of nutrient concentrations Ca, Cu, K, Mg, Mn, Mo, Ni, P, S and Zn (without Fe) in subsoils by sampling location. Sums are given in %wt (10g/kg).

Country	Region	Location	Division	Σ nutrients
Brazil	Paraná	Araucária		0.67
	São Paulo	Registro		0.20
		São Miguel Arcanjo	Filia	0.56
		São Miguel Arcanjo	Matriz	0.36
	Assam	Dibrugarh		4.31
India	Darjeeling	Tinsukia		3.02
		Darjeeling City		2.95
		Darjeeling East		3.11
		Darjeeling North		3.41
		Darjeeling South		3.03
		Darjeeling West		3.05
		Kurseong		3.59
		Kurseong East		3.44
		Mane Bhanjang		2.37
		Mirik		2.96
		Siliguri		2.92
		Teesta Valley		3.43
		Tung		2.96

The soils sampled in the region São Paulo are all deeply weathered latosols (Section 3.2.1). Therefore they show small concentrations of nutrients and show the a strong depletion compared to upper crust. The tea fields in Registro are lowest in nutrients because the fields are located on sandy to silty alluvial deposits (Section 3.2.1). This type of source rock material is generally poor in nutrients, especially if the sand and silt fraction consists mainly of quartzitic grains. The other tea fields in Brazil are slightly less depleted than Registro, probably because the source rocks consisted of minerals with higher contents of nutrients: In São Miguel de Arcanjo the tea fields of the garden's division 'Matriz' are situated on source rock of K-feldspar-rich monzogranite. The tea fields of the division 'Filia' are situated in source rock of Permo-Carboniferous sediments of the Paraná-Basin. The soils of Araucária are derived from migmatic gneisses with biotite-amphibole mesosomes and tonalitic-granodioritic leucosomes, mafic rocks, like amphibolites, and biotite rich, magnesian schists (Section 3.2.2, Sato et al. (2003)). Accordingly, these soils show for several elements greater concentrations in comparison to the other Brazilian soils: For example the large ion lithophile (LIL) elements like K, Rb

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and Ba, typical for TTG suites (Condie 2005), Ni and Co due to the amphibolite lenses and Mg due to the magnesian rich schists. Nevertheless, the nutrient status in the Brazilian is very low and tea soils require intense application of fertilizer and/or compost for commercial tea cultivation (Section 3.2.1).

All subsoils of Darjeeling have approximately similar total content in nutrients. Only for Ca and Mo there is a notably higher spread in the concentrations (Figure 8.1). Although the weathering rate of the source rocks is high due to the subtropical climate conditions, especially in the lower elevations of Darjeeling, the steep slopes with high erosion rates lead to shallow soils with relatively fresh material. This is reflected by less depletion of nutrients compared to the upper crust than the Brazilian soils and accordingly, a much higher total content in nutrients. All soils in Darjeeling are regoliths from the gneisses of the MCTZ and greenschists from the LHS (Section 3.1.1).

The subsoils of the alluvial plain in India, the sampling locations in Assam and Siliguri in Darjeeling, display for most elements a similar geochemical signature than Darjeeling. Only the Ca and Sr concentration are notably greater while the Al and Cs concentrations are notably smaller (Figure 8.1). This shows that the soils in Assam, being fluvial sediments originating from the East-Himalaya, do not significantly weather during their transport from the mountainous parts into the plains of the Brahmaputra river. The higher concentration of Ca could either be an effect of slightly difference in the geological setting of the origin of the sediments or an effect of applying carbonate/dolomite in the sampled gardens.

8.1.2. Comparison between Topsoils and Subsoils

Topsoils and corresponding subsoils have for most elements approximately the same geochemical composition. To identify elements which are influenced by soil management the upper soil volume will be compared with the less influenced, lower soil volume. Figure 8.2 displays the difference between the element concentrations in topsoils and subsoils, subdivided by regions in India and locations in Brazil.

In Assam and Darjeeling there are only very few elements notably different concentrated in top- and subsoils: Ca, P and S are systematically higher concentrated in Indian topsoils than in the subsoils. The heavy metals Cd, Cr and Pb show a wide spread of distribution between topsoil and subsoils. The greater concentration of Ca in topsoils is probably caused by the (irregular) application of carbonate containing rock powder for mitigating the soil pH. The difference of P and S is an effect of the regular application of manure. The elevated S concentration in topsoils could be a result of using compost,

which was enriched with animal feces, e.g. cow dung and chicken feces, or sulphur containing products (personal communication from tea garden managers). Remarkably, other nutrients like K, Mg, Mn or Zn similarly concentrated in the whole soil volume. The greater Cu concentration in the topsoils of same gardens is most probably remnants of copper containing fungicides, which are regularly used in organic farming. The reason for the spread of distribution of heavy metals remains unclear.

In Araucária, Paraná, and São Paulo there is for more elements a significant difference between top- and subsoils: The nutrients Ca and P are strongly enriched in the topsoils. Additionally, the elements S, Na, Ba, Zn, La, Sr, Cu and in Paraná also Y and Cd are found at higher concentrations in topsoils. Partly elevated are K, Mg, Mn, Cr and Cd. The greater concentrations of K, P, Mg, Mn and Zn in topsoils results from the regular application of fertilizers according to USDA standards. Ca, Sr and Ba are probably enriched due to the irregular application of carbonate containing rock powder, similar to Darjeeling and Assam. No reasons could be determined for the differences in distribution between topsoil and subsoil for the named heavy metals and Y.

The differences between topsoils and corresponding subsoils give a qualitative approach about which elements are affected by soil management. These are in strongly weathered soils, e.g. the Brazilian soils, especially P, K and Ca, and with less affected S, Mg, Na, Mn, Ba, Sr and Cu. For less intensely weathered soils, respectively organically treated soils, e.g. the soils of Darjeeling and few in Assam, this affects mainly P and S, and less K, Ca and Cu. The varying distribution of heavy metals in the soil volume have to be taken in consideration for provenance analysis.

The impact of fertilizer and manure application can not be quantified in this study, because the soils had been sampled at only one point of time. Hence, the enrichment factors between topsoil and subsoil in Figure 8.2 must not be used for quantification.

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Figure 8.1.: Element concentrations of subsoils, grouped by tea growing regions and locations in Brazil. Elements are ordered by median of concentrations of all subsoil samples. Median for each sample group is marked by a colored symbol, the shaded areas mark the second and third quartile. Median values are listed in Table 8.2.

Figure 8.2.: Comparison of element concentrations in topsoil versus subsoil, grouped by tea growing regions. Each point represents a pair of topsoil and corresponding subsoil sample. If values are above zero the element is higher concentrated in the topsoil, and if the the values are below zero the element is higher concentrated in the subsoil. Elements are ordered by median element concentration of the subsoils.

Table 8.2.: Topsoil and subsoil concentrations, compilation of data of this thesis and data from H. P. Carr et al. (2003). Elements are ordered by median of subsoil concentrations of this thesis. RMD denotes the median absolute deviation normalized by the median and RSD the relative standard deviation. The compilation of published data is displayed in the columns left of the marker 'Publ.'. Nutrients are marked with an asterix, beneficial elements with a dagger.

	Top:	Median	MAD	RMD %	Mean	SD	RSD %	Sub:	Median	MAD	RMD %	Mean	SD	RSD %
Al [†]		7.4e+04	1.5e+04	21	6.9e+04	2.1e+04	31		8.0e+04	1.1e+04	14	8.0e+04	1.8e+04	22
Fe*		3.8e+04	8.1e+03	21	3.7e+04	1.6e+04	42		4.2e+04	8.5e+03	20	4.3e+04	1.3e+04	31
K*		1.5e+04	9.8e+03	65	1.1e+04	8.7e+03	76		1.9e+04	4.9e+03	26	1.6e+04	8.0e+03	49
Mg*		6.1e+03	4.0e+03	66	5.3e+03	3.6e+03	68		7.0e+03	2.0e+03	28	6.8e+03	4.1e+03	60
Na [†]		2.4e+03	3.5e+03	140	2.9e+03	3.3e+03	110		2.7e+03	3.7e+03	140	3.5e+03	3.1e+03	87
Ca*		2.0e+03	2.0e+03	97	3.2e+03	3.2e+03	100		1.4e+03	1.1e+03	78	2.1e+03	2.5e+03	120
Mn*		5.3e+02	4.6e+02	85	5.7e+02	3.9e+02	69		7.0e+02	3.4e+02	49	7.1e+02	4.1e+02	57
P*		8.0e+02	3.5e+02	44	1.3e+03	1.0e+03	79		6.0e+02	2.5e+02	42	7.3e+02	4.3e+02	60
Ba		3.6e+02	2.8e+02	80	3.6e+02	2.1e+02	57		4.9e+02	1.5e+02	30	4.3e+02	2.1e+02	49
S*		2.7e+02	2.6e+02	93	3.9e+02	3.7e+02	94		1.7e+02	1.4e+02	85	2.5e+02	2.7e+02	110
Rb		1.0e+02	9.2e+01	89	8.8e+01	6.9e+01	78		1.5e+02	5.2e+01	34	1.3e+02	6.7e+01	51
Zn*		7.9e+01	3.0e+01	38	7.6e+01	2.9e+01	38		8.7e+01	2.6e+01	29	8.4e+01	3.5e+01	42
Cr		4.8e+01	3.4e+01	71	7.1e+01	9.2e+01	130		5.6e+01	3.6e+01	64	6.7e+01	5.2e+01	79
La [†]		5.0e+01	1.4e+01	28	4.2e+01	1.6e+01	38		5.4e+01	9.6e+00	18	5.0e+01	1.8e+01	37
Sr		4.6e+01	2.9e+01	62	5.6e+01	4.4e+01	79		4.4e+01	2.8e+01	64	4.9e+01	3.6e+01	72
Ni*		3.1e+01	2.5e+01	80	4.4e+01	5.3e+01	120		3.3e+01	1.3e+01	39	4.1e+01	4.7e+01	110
Cu*		3.0e+01	8.8e+00	29	3.7e+01	3.2e+01	86		3.1e+01	1.2e+01	39	3.5e+01	3.0e+01	87
Li		2.5e+01	2.1e+01	82	2.5e+01	1.6e+01	63		3.1e+01	1.5e+01	48	2.9e+01	1.3e+01	46
Pb		2.2e+01	8.6e+00	39	2.5e+01	2.0e+01	80		2.8e+01	1.1e+01	40	3.3e+01	3.4e+01	110
Y [†]		2.1e+01	1.2e+01	57	2.0e+01	8.7e+00	44		2.7e+01	8.0e+00	30	2.7e+01	1.2e+01	43
Co [†]		1.3e+01	4.3e+00	33	1.3e+01	1.4e+01	110		1.5e+01	5.1e+00	33	1.6e+01	1.2e+01	78
Sc		1.2e+01	2.9e+00	23	1.2e+01	5.8e+00	48		1.4e+01	2.6e+00	19	1.4e+01	5.8e+00	41
Cs		4.2e+00	4.3e+00	100	6.2e+00	5.0e+00	80		9.3e+00	4.7e+00	50	8.6e+00	4.7e+00	55
Mo*		1.0e+00	5.8e-01	56	1.3e+00	1.3e+00	96		9.4e-01	6.2e-01	67	1.1e+00	6.5e-01	61
Tl		5.6e-01	2.3e-01	42	4.5e-01	2.4e-01	53		6.9e-01	8.8e-02	13	6.1e-01	2.2e-01	36
Sb		4.2e-01	2.1e-01	51	4.5e-01	2.4e-01	53		5.3e-01	3.2e-01	61	5.9e-01	3.6e-01	61
Cd		5.7e-02	2.1e-02	36	6.8e-02	3.8e-02	56		3.7e-02	2.9e-02	79	4.8e-02	4.5e-02	93

8.2. Relation between Soil Geochemistry and Shoot Tip Ionome

The relation between ionome of plants and geochemical composition of soils is mostly used to describe the element transfer. This relation is also named 'transfer-factor', 'soil-plant partition coefficient', 'bio-concentration factor', 'concentration ratio', 'enrichment factor' or 'biological accumulation coefficient' (Hope 1995; Roca and Vallejo 1995; Dinelli and Lombini 1996; Rodríguez et al. 2002; Tomé et al. 2003; Chojnacka et al. 2005; Reimann et al. 2007; Goni et al. 2014). In this section the relation of plant to soil is used to I) characterize element subcompositions with similar transfer-factors and II) to identify subcompositions which log-ratios are mostly unaltered by the element transfer from the reservoir (soil) through the plant into the sink tissue.

Figure 8.3 displays the overview of simple vratios between shoot tips and corresponding subsoils. This is the most frequent type of representation for the relation between geochemical composition of soils and the ionome of plants, named 'transfer-factor', 'enrichment factor', etc. It reveals roughly the pattern of element distribution between the subsoils and the shoot tips: The macro-nutrients S, P, K and Ca are generally enriched in shoot tips of *C. sinensis* compared to the corresponding subsoils. Only in Assam Ca is not enriched in the sink tissue. The elements with small transfer-factors are all non-nutrients, micro-nutrients or main elements of the soils: Sc, Fe, REE, Li, Al, Pb, Cr, Co, Sb, Mo, Ba, Cs, Tl, Ni and Cd. For all remaining nutrients and elements with characteristics analogous to a nutrient, Rb, Sr, Mn, Cu, Mg and Zn, it depends on the regions whether the elements are enriched in the sink tissue compared to the subsoils: Especially tea grown on the nutrient-poor soils of Registro and São Miguel de Arcanjo shows greater concentrations in its shoot tips than in the soils.

The vratios of Al are unusual high compared to other plants, because *C. sinensis* is an Al accumulating plant (Section 2.1.3). The vratios for the beneficial REE are in contrast small. Among the non-nutrients the high vratio values of Rb are sticking out; they show similar values like nutrients. As described in Section 7.4, Rb is enriched in the shoot tips compared to the mature leaves resulting into highest concentration of a non-nutrient element in sink tissue (Figure 7.1).

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Figure 8.3.: Simple vratios shoot tip/subsoil of corresponding pairs of samples, grouped by tea growing regions. Elements are ordered by median of vratio. Median for each sample group is marked by a colored symbol, the shaded areas mark the second and third quartile.

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Figure 8.4.: Graph of ilr-ANOVA (CoDa dendrogram) of all shoot tip samples (N = 160) and sub-soil samples (N = 96).

The ilr-ANOVA can be used to group the elements into subcompositions with similar transfer-factors while meeting the requirements of calculating with concentration data (Section 5.1). The graph in Figure 8.4 displays the grouping of element variables if shoot tip samples and subsoil samples from all regions in Brazil, India and Japan are included in the ilr-ANOVA. Six groups can be distinguished:

1. Ca, K, P and S
2. Cd, Cu, Mg, Mn, Ni, Rb, Sr and Zn
3. Ba, Mo and Ti
4. Co, Cs, Na and Sb
5. Al, Cr, Pb and Y
6. Fe, La, Li and Sc

The grouping reflects roughly the order of median simple vrations in Figure 8.3. The first group, the elements Ca, K, P and S, form a subcomposition of elements with similar relation of concentrations between shoot tips and subsoils in respect to all other elements. The bio-availability and thereby the uptake of these elements may be influenced by soil

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management (Section 8.1.2). The second group, the subcomposition of Cd, Cu, Mg, Mn, Ni, Rb, Sr and Zn, consists of elements which concentration in soils is generally less affected by soil management (Section 8.1.2). Depending on the overall situation of the soil the measures of soil management might still have an impact on the uptake of these elements. The uptake of elements of all remaining subcompositions is potentially unaffected by soil management.

The grouping of elements with regard to similarity in the relation between shoot tips and subsoils depends on the used data set. In the following two examples the total data set is split into one data set with samples only from Darjeeling, and in the second data set without the samples from Darjeeling. For both data sets an own ilr-ANOVA is calculated and displayed in CoDa dendrograms.

Figure 8.5.: Graph of ilr-ANOVA (CoDa dendrogram) of shoot tip samples (N=91) and subsoil samples (N=71) of only Darjeeling.

Figure 8.5 shows the grouping of elements for comparing shoot tips and subsoils only from Darjeeling. Most subcompositions are similar to the ilr-ANOVA of the total data set, because the biggest sample group in the total data set are samples from Darjeeling. The most important difference in grouping is regrouping of the nutrient K, which is for Darjeeling in the second group. This confirms the results from Section 8.2, that soil management in Darjeeling has only a very minor impact on K concentration in soils.

Figure 8.6 shows the grouping of elements for comparing shoot tips and subsoils

Figure 8.6.: Graph of ilr-ANOVA (CoDa dendrogram) of shoot tip samples (N = 69) and subsoil samples (N = 25) from all regions except Darjeeling.

without samples from Darjeeling. The first and second group are corresponding to the ilr-ANOVA of the total data set, only Ni belongs to an other group. All other element variables are differently grouped into to two groups: A third group of Ba, Cs Ni, Na and Tl, and a fourth group of all remaining elements. This dendrogram exhibits an apparent difference between elements which are are potentially influenced in their uptake by soil management and and the agricultural 'uninteresting' elements. Especially the third and fourth subcomposition is potentially important for provenance analysis.

One preparation step for provenance analysis is to identify subcompositions which remain stable in their log-ratios during the uptake process from the element reservoir to the sink tissue. These subcompositions can be determined by comparing the distribution of pairwise log-ratios between shoot tips and corresponding soils. The results are calculated as well for topsoils as for subsoils, because for some tea growing regions geochemical composition of topsoils and subsoils have to be considered. The heatmaps of the Figures 8.7 and 8.8 display the results of the comparison between the log-ratio distributions.

Topsoils and corresponding shoot tips have following comparable log-ratio distributions:

- K, P, K~S and K~Ca having p-values slightly below 0.05

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Figure 8.7.: Heatmap of p-values calculated by paired Student's *t*-test between distribution of pairwise log-ratio of shoot tip samples versus corresponding topsoils. Total number of sample pairs $N = 33$, with Darjeeling $N = 13$, Assam $N = 6$, São Paulo $N = 9$ and Paraná $N = 5$. P-values of log-ratios of element pairs are colored blueish if they are below 0.05 (alternative hypothesis: true difference in means is not equal to 0) and are colored greenish to yellowish if values are above 0.05 (the means of two populations are equal).

- Cu, Mg, Mn, Rb, Zn with Zn~Sr, and without Zn~Mn and Zn~Rb.
- Cd, Sr and Ni~Cd
- Co, Cr, Mo, Pb, Sb with Cs~Sb, Cs~Mo, Al~Pb and Al~Co, but without Pb~Sb, Pb~Mo, Co~Sb and Co~Mo
- La, Fe
- Li, Y
- Ba, Tl

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Figure 8.8.: Heatmap of p-values calculated by paired Student's *t*-test between distribution of pairwise log-ratio of shoot tip samples versus corresponding subsoils. Total number of sample pairs $N = 81$, with Darjeeling $N = 59$, Assam $N = 6$, São Paulo $N = 11$ and Paraná $N = 5$. P-values of log-ratios of element pairs are colored blueish if they are below 0.05 (alternative hypothesis: true difference in means is not equal to 0) and are colored greenish to yellowish if values are above 0.05 (the means of two populations are equal).

Subsoils and corresponding shoot tips have following comparable log-ratio distributions:

- Cd, Mg, Rb, Sr, Zn with Cd~Cu
- Mn and Cu
- Cs, Mo, Sb with Mo~Tl
- Co, Cr, Pb with Co~Al
- Fe and La

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The subcomposition Cd, Cu, Mg, Mn, Rb, Sr and Zn as similar log-ratios within the subcomposition between shoot tips and corresponding soils, as well topsoils as subsoils. Except for Rb, Sr and Cd the elements are all nutrients. For several of the elements there are differences between topsoil and subsoil (Figure 8.2), especially for Cu, Mn, Sr and Zn, leading to less comparability between subsoils and shoot tips compared to topsoils and shoot tips (Figure 8.8). Nevertheless, the element ratios within this subcomposition of shoot tips seem to generally reflect the respective element ratios in the total soil volume. Tyler (1997) describes a similar finding for Rb in acid soils, such as tea soils are.

The subcomposition Co, Cs, Mo, Na and Sb, combined with Al, Cr and Pb is a second subcomposition where the pairwise log-ratios between shoot tips and topsoils and subsoils are comparable. Of these elements, only Mo and Co are (micro)-nutrients. Accordingly, the uptake of these elements occurs probably due to poor ion differentiation by transporter proteins rather than specific uptake. Interestingly, the log-ratios of Al~Co are similar between the shoot tips and both, topsoils and subsoils. Al is by some authors described as a beneficial element for *C. sinensis* (Section 2.1.3). The data suggest, that the uptake of the beneficial elements Al and Co into the sink tissue of *C. sinensis* is linked to the Al to Co ratio in the soil.

The subcomposition Ca, K, P and S is composed of elements of which the tea plant has high demand and which bio-availability can be strongly influenced by soil management (Section 8.1.2). The pairwise log-ratio comparison shows that the log-ratios of these elements in shoot tips are similar to the log-ratios of the corresponding topsoils, but not to the corresponding subsoils. As expected, this shows that the soil management has a major influence on the concentrations of Ca, K, P and S in shoot tips.

Only log-ratios with Ba are always different between shoot tips and corresponding soils. On the one hand, this could be an effect of varying element translocation inside the tea plant (Section 7.4.1, Figure 7.7). On the other hand, it could be an effect of differences in the Ba uptake into the plant, which is not yet very well understood or discussed in the bibliography, up to the author's knowledge.

The remaining subcomposition Sc, Li, Ti, Fe and REE, is characterized by poor uptake of the plant. These are also all elements which can be strongly affected by APs (Chapter 6 and Figure 6.5). Although the data of the shoot tip samples had been corrected for adhering particles interpretation of log-ratios with these elements should be done with caution, e.g. through propagating the respective errors (Section 6.4).

8.3. Summary

The geochemical composition of subsoils is similar between all tea soils in respect to the elements Al, Fe, P and Sc and less similar to the elements Zn, Cr, Pb and Cd. The composition is different in respect to the elements S, Cs, Ca, Na, Sr, Rb, and K. The Brazilian soils are stronger depleted in these elements than the Indian soils, except for S. The deeply weathered soils in Brazil are very poor in nutrients. The soils of Assam and Darjeeling show approximately four times greater nutrient concentrations. These differences are caused by the geochemical composition of the geological source rocks and the specific weathering and erosion patterns.

The geochemical contrast between topsoils and corresponding subsoils give a qualitative estimation about which elements are affected by soil management. In the deeply weathered soils of Brazil the concentrations of P, K and Ca, are strongly affected by measures of soil management, and S, Mg, Na, Mn, Ba, Sr and Cu are less affected. The concentrations of the elements P and S are both strongly affected in less intensely weathered soils, respectively organically treated soils, e.g. the soils of Darjeeling and few locations in Assam. K, Ca and Cu are less affected in these soils. The varying distribution of heavy metals between topsoils and subsoils has to be taken in consideration for provenance analysis.

The macro-nutrients S, P, K and Ca are generally enriched in shoot tips of *C. sinensis* compared to the corresponding subsoils. Only in Assam Ca is not enriched in the sink tissue. The elements with small transfer-factors are all non-nutrients, micro-nutrients or main elements of the soils: Sc, Fe, REE, Li, Al, Pb, Cr, Co, Sb, Mo, Ba, Cs, Tl, Ni and Cd. For all remaining nutrients and elements with characteristics analogous to a nutrient, Rb, Sr, Mn, Cu, Mg and Zn, it depends on the regions whether the elements are enriched in the sink tissue compared to the subsoils: Especially tea grown on the nutrient-poor soils of Registro and São Miguel de Arcanjo shows greater concentrations in its shoot tips than in the soils.

The elements can be grouped by similarity of their transfer-factors (based on ilr-ANOVA): One group consists of Ca, P, S and - if samples from Darjeeling are omitted - also in K. A second group consists in Cd, Cu, Mg, Mn, Ni, Rb, Sr and Zn, and in Darjeeling also in K. All other elements can be subsumed into one large group with several sub-groups, depending on the data set which was used to calculate the ilr-ANOVA.

There are two subcompositions which show statistically stable log-ratios during the uptake process from the element reservoir to the sink tissue: The subcomposition Cd,

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Cu, Mg, Mn, Rb, Sr and Zn and the subcomposition Co, Cs, Mo, Na and Sb, combined with Al, Cr and Pb. The log-ratio distributions of the subcomposition consisting of K, Ca, S and P are similar only between the topsoils and the shoot tips.

In summary, the uptake of the elements Ca, S, P and in some cases K might be strongly influenced by the soil management and therefore, these elements are not suitable to be linked to the geological source rock. They can serve as a proxy regions with very low fertility status of the soils and/or for regions with very intensive tea cultivation. In Darjeeling uptake of K does not seem to be notably altered by soil management, probably because most tea gardens are submitted to organic cultivation. Log-ratios of elements of the subcomposition Co, Cs, Mo, Na and Sb, Al, Cr and Pb can be correlated to the geochemical composition of the total soil volume and are under this aspect suitable for provenance analysis. The subcomposition Cd, Cu, Mg, Mn, Rb, Sr and Zn, consisting of nutrients and replacement elements, correlates well with the subsoil composition and is therefore suitable for provenance subcompositions which discriminate between geological source rock material.

9. Provenance Analysis

In this thesis provenance analytics for tea is solely based on the ionome of the leaves. Previous publications showed that geographic discrimination of tea by element concentration is possible (Marcos et al. 1998; Fernández-Cáceres et al. 2001; Moreda-Piñeiro et al. 2001, 2003; Kelly et al. 2005; Q. Chen et al. 2009; Gonzalvez et al. 2009; Pilgrim et al. 2010). The emphasize of this chapter lies on the questions why the samples can be discriminated into geographical regions and which element subcompositions are suitable to geographically discriminate which groups of tea samples. To achieve this, the statistical provenance analysis is embedded into the framework established in the preceding chapters: The provenance is determined on basis of the 'robust' subcompositions constituted of those elements which are less affected by parameters of the tea production, such as soil management, harvesting methods, machinery or contamination by adhering particles.

The chapter will not cover a holistic model for world spanning provenance analysis of tea. As discussed in the previous chapters, the processed tea ionome is influenced by a) parameters which potentially change between seasons and b) parameter which can be treated as constants, because they are changing very slowly or change only in decades. The parameters being supposedly constants are the geological source rock, the geochemical composition of subsoils, the type of plant, seed plant, hybrid/cultivar, and the long-term climate. The parameters submitted to potentially high fluctuation are weather conditions of the respective season, soil management, like fertilizer, weeding, etc. and tea production, including shading, the plucking standard, leaf grading and used machinery for the different type of teas. The latter parameters can also significantly contribute to determining a provenance of a processed tea sample, because each tea growing region has its specific traditions and preferred tea production methods. A holistic model would include an interlacing of various statistical methods applied on the respective parameter-specific subcompositions to increase the probability of tea sample classification. For example, in the mountainous part of Darjeeling only orthodox black tea and special type of green tea is produced. In Assam nearly the whole tea produc-

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tion is specialized in CTC black tea manufacturing, and only very minor quantities of the harvest is manufactured differently. Accordingly, the results of an analysis based on a metal subcomposition to distinguish between CTC and non-CTC production could serve as a-priori value for discriminating teas from Assam and Darjeeling. Several other methods and techniques preceding the final discrimination step had been proposed, e.g. by Moreda-Piñero et al. (2001) and McKenzie et al. (2010) and Gonzalez et al. (2009, and references therein). A holistic model which includes several classification techniques in order to make the provenance analysis more robust and reliable in terms of the changing parameters of tea production is a research topic, respectively developing task, on its own.

Keeping the size of the total data set in mind, provenance analysis in this chapter is purposely based only on discrimination methods. In particular LDA has been used in this thesis. A powerful ability of this linear method is to clearly picture the influence of the variables, elements in this case, on the probability of samples to which sample group they belong to. Other, more advanced techniques, like probabilistic neural networks (McKenzie et al. 2010) or soft independent modeling of class and analogy (Moreda-Piñero et al. 2001), require larger data sets or larger samples subgroups for satisfactory results.

In the previous chapters subcompositions had been determined which are either sensitive or insensitive in respect to a tea cultivation or production parameter. It allows to rate for each element how intensely its concentration is altered by a single parameter or a combination of the parameters. Additionally, the rating is weighted based on field observations and personal communications with tea producers, traders and scientists. The combination of rating and weighting is a qualitative approach to express the robustness of each element in terms of a specific tea cultivation and production step as integer value (Table E.1): Elements with high values have a small probability to be affected by the tested parameter. For the relation tea/soil the scale is reverse; elements which show similar log-ratio distributions between shoot tip and soil have high rating-values. Thus, the sum of the values provides a qualitative criterion how suitable an element is to be used in a subcomposition which is designed to capture in the ionome the geochemical composition of the parent material of the soils. Such a subcomposition can be used to discriminate teas which had grown on contrasting soils, because the influence of tea cultivation and production parameters is minimized. The element list sorted from high suitability to low suitability is Mn, Rb, Cs, Sr, Co, Zn, Cu, Sb, La, Mg, Tl, K, Cd, Pb, Mo, Cr, Al, Y, Ni, Li, Fe, Ca, P, Na, S, Ba, Sc (Table E.1). One task of a holistic model would

be to establish a index of robustness entirely based on statistical analysis on a larger and more balanced data set. Most probably, this would also lead to a slightly different index of robustness than the qualitative approach.

In this thesis the tea provenance studies are based on subcompositions which are selected by their general suitability, respectively robustness, and less by their discriminative power in this specific data set. This contrasts with, to the author's knowledge, all published tea provenance studies, where the set of variables for the discrimination functions is selected by statistically determining the most discriminating variables of the respective data set. To show the principles of this 'robustness-approach' three case studies are presented with varying categorical variables: 1) Discrimination by countries, 2) discrimination by regions in India and 3) discrimination by geological metamorphic zones in Darjeeling. The six elements with the highest suitability/robustness rating are used as the 'standard' subcomposition: Mn, Rb, Cs, Sr, Co and Zn. This standard subcomposition will be altered by few elements to achieve a better discrimination according to knowledge about the local specifics. All samples are filtered for their approximated average leaf development stage (Section 7.4.2). The balance [Cu K | Al Ca Mn] of all samples has values between -1.2 to 0.5. This homogenization of samples in terms of their average leaf age allows to use for example Cu, K, Al, Ca and Mn in subcomposition for discriminating between regions. The linear discrimination is applied on ilr-transformed data.

9.1. Countries

The data set comprises samples of three countries: Brazil, India and Japan. Most tea production parameters vary between the countries. Additionally samples from India span the three very different tea growing region Darjeeling, Assam and Nilgiris. Applying the LDA on the pre-defined element subcompositions with the countries as categorical variable indicates which parameters do not discriminate between the countries, and which parameters could serve as proxies of origin.

Figure 9.1 displays the results of a LDA on the ilr-transformed data set of 231 samples and six elements (five ilr-variables). The three sample groups can be separated through log-linear combinations of these six elements, but the groups show an overlapping by several samples. The misclassification rate is lowest for India with only 6 of 183 samples wrongly classified as Japanese samples (Table 9.1). For Japan the misclassification rate is 37.5% with 6 samples classified to India, and for Brazil 30.8% with 12 samples

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classified as Indian samples. Samples from Brazil and India are separated mainly along the LD1-axis and samples from Japan can be discriminated from Brazilian and Indian samples along the LD2-axis. Looking at the values of the clr-scalings (Table 9.1) the Brazilian samples differ from Indian samples by relatively higher concentrations of Cs Mn and Zn compared to Rb, Sr and Co. The Japanese samples differ from Brazilian and Indian samples by relatively higher concentrations of Mn, Zn and Rb compared to Sr and Co.

Figure 9.1.: Scatter plot of tea samples displaying the first two scores of linear discriminant functions for origin by countries. Samples are colored by country and the label denotes the sampling location of the shoot tips. Processed tea samples are labeled with 'T'. Total number of samples is N = 230 (India N = 183, Brazil N = 39, Japan N = 16). Clr-scalings for LD1 and LD2 and misclassifications are listed in Table 9.1.

The relatively higher Mn, Zn and Rb concentration in Japanese samples could be an effect of the originally igneous source rock material of the soils. The samples of Brazil plotting into the field of the Japanese samples originate from the sampling locations B-30 to B-33 of the garden Yamamotoyama do Brasil, Araucaria (Araucaria), with medium LD1 and LD2 values. These locations are situated on the hornblende-rich, tonalitic

Table 9.1.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea by countries. Table corresponds to Figure 9.1). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Mn	Rb	Sr	Zn
LD1	0.51	-1.34	-1.17	1.81	0.45	-0.27
LD2	-0.32	0.08	1.00	0.23	-1.64	0.65

	Brazil	India	Japan
Brazil	28	11	0
India	1	174	7
Japan	0	6	10

gneisses of the Atuba-Complex, which include frequently lenses of amphibolites (Section 3.2.2). The other location of Araucaria, B-35, is situated on local, alluvial sand deposits (Figure A.10). Although this sampling location is only 600 m north of B-33, and all shoot tip samples from this garden have exactly the same growing conditions, this sample plots closer to all other Brazilian samples. The Indian samples 284 (UPASI, research field of South Indian Tea Association (UPASI)), 294 (Havuka1) and 295 (Warwick Tea Estate (Warwick)), which also have high LD2-values, originate from the East-Nilgiris with source rock of a charnockite suite (Section 3.1.3). The charnockite formations of this area contain pyroxene granulites and doleritic dykes. Hence, one parameter constituting the LD2-function is probably mafic source rocks as parent material for the tea soils.

The selected subcomposition of Mn, Rb, Cs, Sr, Co and Zn is - from a geochemical point of view - not the most suitable selection to serve as a reliable proxy for mafic source rock for the tea plantations. A better selection includes Ni, Mg and Fe, which are together with Co and Mn connected to the Fe-bearing phases, e.g. altering minerals like pyroxenites and amphibolites. The biplot in Figure 9.2 is based on clr-values calculated by the subcomposition Mn, Rb, Cs, Sr, Co, Ni, Mg, Fe and Li. In this plot the labels of the elements Fe, Ni and Mn are projected into one line. This indicates that the log-ratios of these three variables have a good correlation among them, i.e. that these elements are mostly controlled by the same processes. A second set of presumably co-depending elements are Mn, Zn and Mg. Additionally, all shoot tips with high log-ratios of Mn, Co and Ni compared to other elements are grown on soils which parent material contained mafic minerals, e.g. the hornblende-biotite gneiss or charnockites (right side of Figure

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Figure 9.2.: Clr-biplot of tea ionomes of leaf samples for subcomposition Mn, Rb, Cs, Sr, Co, Ni, Mg, Fe and Li. Total explained variance is 0.62. Total number of samples is N = 230 (India N = 183, Brazil N = 39, Japan N = 16). Labeling of samples is according to their geological source rock, or if information of those are missing, their sampling point. Abbreviations are: H+BG hornblende+biotite gneiss, G+MG garnet+muscovite gneiss, S+GG staurolite+garnet gneiss, StG staurolite gneiss, H+BM hornblende+biotite monzogranite, Chrn charnockite, Allv alluvium of Brahmaputra river, flvs fluvial sediments, Prns sediments of the Paraná Basin, T processed tea samples, others: labels of sampling points.

9.2). Shoot tips grown on fluvial sediments have the smallest log-ratios of Mn, Co and Ni compared to other elements (left side of Figure 9.2). These results are a strong indicator that the Mn, Ni and Co concentration in *C. sinensis* are caused by altering mafic minerals. In the present data set Co and Mn may also alone serve as proxy for mafic source rocks.

The Brazilian tea samples plotting into the 'Brazilian' field are all grown on sediments as source rock. In the area of Registro (points B-7 – B-23) the outcrops are described as slightly immature, sandy to silty alluvial deposits (Section 3.2.1). In combination with the high weathering rates in the sub-tropical climate the soils are depleted in all major cations (Table 8.1). Most samples of the other Brazilian regions are grown on sedimen-

tary source rock, except for the points B-30 – B-33 and B-55 – B-57, as described in the previous paragraph. In total 16 samples originate from sediments, 8 from gneiss and monzogranite, and 15 are processed tea samples. The LD1 function, which discriminates between Brazilian and Indian samples, is dominated by Rb versus Cs and Mn (Table 9.1). For this data set, it suggests that element uptake from sandy to silty sediments of Rb versus Cs is fundamentally different in Brazil than from soils of Japan or India. This is probably not only caused by the characteristics of the geological parent material, because the tea soils of Assam are also developed from alluvial sediments. It could be an combined effect of the geochemistry of source rock, soil types, fertilizer/manure/carbonate application, and cultivar. The latter parameter obviously has only a minor impact on the regional discrimination, because most samples of Japan are the same cultivar - *C. sinensis* 'yabukita' - as sampled in B-54 to B-60 in Brazil. In summary, it remains unclear whether the discrimination between Brazilian and Indian samples is purely an effect of the sedimentary source rock or rather an interaction of soil management meeting very different soil types.

The results of the LDA with the standard element subcomposition, Mn, Rb, Cs, Sr, Co and Zn, exhibit that this subcomposition is suitable to distinguish tea samples roughly by country and by their geological source material. In some cases the fingerprint of the geological background superimposes other, regional geochemical signals caused by differing tea production systems. To enhance the discrimination between countries the element subcomposition has to be increased by elements which capture local specifics: Brazilian tea garden management includes intense fertilizer application (Section 8.1.2) and therefore K and P are included into the subcomposition. Several Japanese samples showed a significantly higher concentration of Li than the average ionome of tea (Figure 7.1 and 9.2) and therefore Li is added, too. The results of the LDA with the subcomposition of Mn, Rb, Cs, Sr, Co, Zn, K, P and Li are displayed in Figure 9.3. In this scatter plot the samples groups are notably better discriminated than in Figure 9.1. Only eight samples of Brazil (*Araucaria*), two samples of India, and one sample of Japan, can not be classified into their respective group (Table 9.2). That shows that these three additional elements help to significantly improve the discrimination between the groups. Only the plants originating from mafic source rocks are still misclassified by this combination of variables and method. For a further refinement of discrimination between Brazilian and Indian samples one could either use a different, more specified set of variables, a-priori values derived from a different analysis, or a larger data set which would allow to include more variables and/or different statistical techniques.

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Figure 9.3.: Scatter plot of tea samples displaying the first two scores of linear discriminant functions for origin by countries, including the elements K, P and Li. Samples are colored by country and the label denotes the sampling location of the shoot tips. Processed tea samples are labeled with 'T'. Total number of samples is $N = 231$ (India $N = 176$, Brazil $N = 39$, Japan $N = 16$). Clr-scalings for LD1 and LD2 are listed in Table 9.2.

Table 9.2.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea by countries. The element compilation includes K, P and Li. Table corresponds to Figure 9.3). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Mn	Rb	Sr	Zn	K	P	Li
LD1	0.44	-0.77	-0.61	1.26	1.09	1.70	1.61	-4.21	-0.50
LD2	0.02	-0.81	-0.23	1.15	-1.28	-0.13	1.07	-0.41	0.62

	Brazil	India	Japan
Brazil	31	8	0
India	1	181	1
Japan	0	1	15

9.2. India

Figure 9.4.: Scatter plot of shoot tip and processed tea samples displaying the first two scores of linear discriminant functions for origin by regions of India. Samples are colored by region and the label denotes the garden of origin. Total number of samples is $N=183$ (Darjeeling $N=136$, Assam $N=26$, Nilgiris $N=21$). Clr-scalings for LD1 and LD2 and misclassifications are listed in Table 9.3. Abbreviations are for Nilgiris: PI Palaniappa, U UPASI, W Warwick, Hg Highfield, Hv Havukal, KK Kil Kotagiri, Nn Nonsuch.

The shoot tips and processed tea ionomes of Indian samples display in Figure 9.1 and Figure 9.3 a certain spread, but no distinct subgroups can be seen. To discriminate the regions of India the standard subcomposition Mn, Rb, Cs, Sr, Co and Zn is used, identical to the LDA in the previous section. Here, the three tea growing regions of India are taken as categorical variable for the LDA: The regions Darjeeling and Assam can not be distinguished by the standard subcomposition (Figure 9.4) and the misclassification table gives only a 35 % correct classification for Assam (Table 9.3). Samples from Nilgiris display a large spread, as well along the LD1 axis as along the LD2 axis, but they can be discriminated from the other two regions with a misclassification rate of 24 %.

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Table 9.3.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea by tea growing regions in India. Table corresponds to Figure 9.4). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Mn	Rb	Sr	Zn
LD1	0.99	-0.22	0.09	-1.35	-0.14	0.62
LD2	0.47	-0.72	0.70	1.56	-0.93	-1.08

	Assam	Darjeeling	Nilgiris
Assam	9	17	0
Darjeeling	0	135	1
Nilgiris	1	4	16

The discrimination between tea samples from Nilgiris versus Darjeeling and Assam is controlled by the LD1 axis. The grouping is mainly achieved by log-linear combination of Co and Zn versus Rb. The samples from Nilgiris show greater values for Co and Zn in respect to Rb.

There are several possible reasons why log-ratios of Co and Zn versus Rb discriminate between Nilgiris and North India: The parameter of cultivars does obviously not induce a visible bias on discrimination by regions: The sample of Warwick consists in leaf material of a popular cultivar of Darjeeling, the 'AB2' clone; the other samples from Nilgiris, consisting in leaf material of cultivars and plants grown from seeds of *C. sinensis* var. *assamica*, are comparable to Assam. Nilgiris and North India differ in their climatic conditions, eg. by the monsoon pattern (Section 3.1.3). The impact of climatic parameters on geographical discrimination can not be quantified, and although it might be a notable factor for varying element uptake by *C. sinensis*, will not be discussed further on. The soils in Nilgiris are very deep with laterite subsoil and show poor nutrient status (Section 3.1.3). Therefore, most tea gardens in the Nilgiris rely on conventional soil management with regular and in cases intense usage of fertilizers (personal communication of UPASI Tea Research Foundation). Only few gardens are certified organic, e.g. Korakundah, United Nilgiri Tea Estates (Korakundah) (not sampled), or even under conversion, e.g. Highfield, or used to be organic, e.g. Palaniappa Tea Estate (Palaniappa). The samples of Darjeeling and Assam originate mainly from organic tea gardens, and soils are less intensely weathered.

In summary, the tea producing area Nilgiris exhibits a quite different setting than the northern areas, with deep, lateric soils, different monsoon pattern and contrasting source

rock material. In Nilgiris, the soil management might have more impact on the bio-availability of elements than in e.g. in Darjeeling, where the roots of *C. sinensis* easily reach (in)to the solid rock. But Co concentration is improbable to be directly influenced by tea management, because there are no recommendation for Co-applications for tea in Nilgiris (Durairaj et al. 2015). Therefore, the relatively higher Co concentrations in the tea leaves are probably an effect of the basement rock, the charnockite suite of the Nilgiri Massif. This would point towards the same interpretation for Co concentration as in the preceding section. Hence, Nilgiris samples can most probably mainly be distinguished from other regions by elements which serve as indicators to the specific, quite unique geological setting of the area. The discrimination will gain robustness if the chosen subcomposition are combined with fertilizer indicators and indicators for the laterization of soils: The aim should be to capture the contrast between the characteristics of the soils and the soil managements.

Table 9.4.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea by tea growing regions in India. The element compilation includes K and Mg, and excludes Mn. Table corresponds to Figure 9.5). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Rb	Sr	Zn	K	Mg
LD1	0.85	-0.25	-1.32	-0.20	0.52	2.21	-1.81
LD2	0.35	-0.40	0.54	-1.47	-2.17	-1.12	4.27

	Assam	Darjeeling	Nilgiris
Assam	12	14	0
Darjeeling	4	132	0
Nilgiris	0	2	19

To exemplary show how to capture the contrast between the soils by this small data set only two indicator elements are added: The element K is added to the standard subcomposition to capture fertilizer application and Mg is added to capture the contrast of laterization of soils between the regions. The element Mn had been excluded, because it plays no significant role for the discriminant functions (Table 9.3). The result of the LDA with the subcomposition of seven elements (six ilr-variables), Ca, Cs, Rb, Sr, Zn, K and Mg, is displayed in Figure 9.5. Adding the two indicator elements results into a better classification of samples from Nilgiris in comparison with samples from North India (Table 9.4, lower table) then of without them (Figure 9.4).

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Figure 9.5.: Scatter plot of shoot tip and processed tea samples displaying the first two scores of linear discriminant functions for origin by regions of India, including the elements K and Mg. Samples are colored by region and the label denotes the garden of origin. Total number of samples is N=183 (Darjeeling N=136, Assam N=26, Nilgiris N=21). Clr-scalings for LD1 and LD2 and misclassifications are listed in Table 9.4. Abbreviations are for Nilgiris: PI Palaniappa, U UPASI, W Warwick, Hg Highfield, Hv Havukal, KK Kil Kotagiri, Nn Nonsuch.

As before, the regions can be separated along the LD1 axis. This log-linear combination of elements is characterized roughly by K, Zn and Co versus Sr, Rb, Cs and Mg. The high LD1 values of samples from Nilgiris can be interpreted as that they are relatively higher concentrated in K, Zn and Co versus Sr, Rb, Cs and Mg than samples originating from Darjeeling or Assam. A possible source for high Co values could be the source rock material, as discussed in preceding paragraphs. High K concentrations are presumably caused by fertilizer application, like the recommended mixtures with muriate of potash KCl (Durairaj et al. 2015). A possible source of Zn are foliar sprays of Zinc sulphate, which is recommended to be applied four to six times every year. Both these treatments are not permitted for certified organic gardens, like most gardens in

Darjeeling are. In contrast, the lateritic, acidic soils would be strongly depleted in soil bases, like Sr, Rb, Cs and Mg. There are no soil data of Nilgiris included in the data set, but, by field observation the soils of Paraná are similar to the soils in Nilgiris. Figure D.2 shows that the soils of Darjeeling and Assam are far less depleted in Mg, Sr, Cs and Rb than the soils of São Paulo and Paraná. The comparison of geochemical composition of shoot tips with corresponding subsoils in Section 8.2 shows that subcomposition Mg, Rb and Sr and the subcomposition Cs with Sb have similar log-ratios in soils and shoot tips (Figure 8.8). Resuming these findings, the low LD1-values of tea samples from Darjeeling and Assam are caused by their 'young' soils in contrast to the deeply weathered soils of Nilgiris.

The two misclassified samples of Nilgiris, point 288 in Highfield and point 301 of Palaniappa are both sampling locations where the soils are treated organically. In Highfield it was a section which was under conversion for several years, and in Palaniappa the section had been recently reactivated after several years of being overgrown. Both situations could lead to poor K content in the soil solution (no fertilizer) and slightly elevated bio-availability of Sr, Rb, Cs and Mg through increased organic content (compost, forest litter). This shows that a discrimination of tea samples originating only from organic tea gardens of Nilgiris and Darjeeling would require a subcomposition which is more specific to separate Indian tea grown on lateritic soil versus other soil types.

In summary, samples of Nilgiris can be discriminated from samples of Darjeeling and Assam due the contrasting soil geochemistry and the consequential soil management. The reasons for the spread of Nilgiris samples along the LD2 axis can not clearly be determined. There is no obvious pattern by geographical location. In Pilgrim et al. (2010) the authors have shown that samples of the Nilgiris can be separated by different tea gardens. In this publication the discrimination seems to roughly follow the geographical pattern, that samples from East and West Nilgiris plot into different groups. In contrast, in the present data set the values of the log-linear combination of LD2 points towards an influence of the conventional versus organic/integrated tea garden management: Clearly conventional gardens, like Nonsuch Estates Pvt.Limited (Nonsuch), Kil Kotagiri, Havukal, Warwick and UPASI have notably lower LD2-values than organic or gardens under conversion like Palaniappa¹ and Highfield.

The discrimination of tea samples from Darjeeling and Assam requires a more spe-

¹Palaniappa is technically neither organic nor under conversion, but had been organic until recently, and the manager of the tea garden tries to use as less conventional products as possible (as of 2015)

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cialized subcomposition, because the soil parent material and cultivation (organic/conventional) is similar for both sample groups. The data set of Darjeeling and Assam contains mostly samples from organic gardens and the soils are constituted of material derived from the Himalaya (Section 3.1.2). As described in Section 8.1.1 the geochemistry of Darjeeling and Assamese soils is very similar. The differences in the plantation setting are a) soils depth: soils in Darjeeling are partly very shallow, and roots are intruding into the solid rock, b) topography: Darjeeling is characterized by steep slopes and good drainage, while Assam is characterized by flat landscape and a drainage system is mandatory to reduce water-logging (Kabir and Das 2015), c) transport distance of source material for soils: the sediments in Assam had been transported by the river Brahmaputra, d) climate, and e) different cultivars.

To discriminate between samples from Assam and Darjeeling the subcomposition should therefore include elements which uptake is sensitive to rhizosphere - solid rock interaction, sensitive to water-logging and/or sensitive to the transport distance of source material of the soils. Elements which uptake is sensitive with respect to the climate and cultivar cannot be determined because the data set is inadequate for this purpose. As discussed in Section 7.2, an increased Al uptake could be one of the indicators for the plant's reaction to poor nutrient bio-availability, e.g. if the plant locally reduces the pH around the feeder root apex to mobilize nutrients from more stable phases. Regular occurring floods and seasonal changing groundwater level - like in Assam - contribute to changing Eh-pH conditions in varying soil depth. For certain elements this has a major impact on their mobility in the soils. Mn is one of the elements which mobility is sensitive to Eh-pH conditions in acidic soils and with very good suitability for provenance on tea. But obviously it has no discriminating power for tea samples from Assam and Darjeeling (Table 9.3). An other candidate element is TI, because it is general well suitable for provenance (Table E.1) and its mobility is sensitive to changing Eh-pH conditions.

It has to be noted that the mobility of TI in soils is still a matter of ongoing research (Grösslová et al. 2015, and references therein). Generally TI is described to have geochemically an analogous characteristics to K. Illite clays as well as Mn- and Fe oxides and hydroxides are well known to have an fixating effect on TI (Kabata-Pendias 2010; Vanek et al. 2011). Also, the sorption of TI to soil organic matter (SOM) under reducing conditions is suggested to be a important parameter controlling TI bio-availability (Kabata-Pendias 2010; Grösslová et al. 2015, and references therein). Soils in Assam are described to have high content in TOC and the dominant clay mineral is illite (Section 3.1.2). The regular occurring floods and seasonal changing groundwater level contribute

to changing Eh-pH conditions in varying soil depth.

Figure 9.6.: Clr-biplot of soils from Darjeeling and Assam for the subcomposition Al, Ca, Co, Cs, Fe, K, Mn, Rb, Tl and Zn. Total explained variance is 0.77. Total number of samples is $N = 103$ (Assam $N = 13$, Darjeeling $N = 90$).

The total content of Tl and Al in the soils of Assam and Darjeeling has most probably no influence on the uptake. The clr-biplot in Figure 9.6 displays that the log-ratios of Al, Fe and Tl have a very small spread between all soils. The main difference between the soils is the significantly higher Ca concentration in Assamese soils compared to Darjeeling (Figure 8.1). Supposedly, the Ca content increases the pH in the soils of Assam which would reduce the uptake of Al (Section 2.1.2). The role of CaCO_3 for Tl uptake is discussed diversely: On the one side CaCO_3 hampers the mobility of Tl in soils (Vanek et al. 2011), on the other it could an important source to Tl (Grösslová et al. 2015). Because the source of the Ca in the soils of Assam is unknown, it could be either through the sediment material or the carbonate/dolomite applications, its implication for the Tl uptake remains unclear.

Nevertheless, Figure 9.7 and Table 9.5 show that adding Al and Tl to the standard sub-

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Figure 9.7.: Histogram of shoot tip and processed tea samples displaying the first score of linear discriminant function separating Darjeeling and Assam. The subcomposition includes the elements Al and Tl, and excludes Sr. Samples are colored by Subgroup. Total number of samples is $N = 162$ (Darjeeling $N = 136$, Assam $N = 26$). Clr-scalings for LD1 and misclassifications are listed in Table 9.5.

Table 9.5.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea from Assam and Darjeeling. The element compilation includes Al and Tl, and excludes Sr. Table corresponds to Figure 9.7). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Mn	Rb	Zn	Tl	Al
LD1	-0.86	1.06	-0.32	-0.94	1.19	-1.29	1.16

	Assam	Darjeeling
Assam	22	4
Darjeeling	5	131

composition a LDA separates the samples reasonable well according to their respective groups. Sr is excluded from the subcomposition because it is no discriminating element in this log-linear combination. The LD1 is characterized by roughly Al, Zn and Cs versus Ti, Rb, Co and Mn. As expected, the positive Al values helps to discriminate Darjeeling from Assam and the negative Ti values Assam from Darjeeling. The higher Ti concentrations in shoot tips from Assam compared to Darjeeling (Figure 7.1) could therefore be caused by a complex interaction of illite, SOM, water-logging and soil acidity controlling the mobility of Ti.

In summary, tea from Darjeeling can be discriminated from Assam despite very similar soil geochemistry. Elements which uptake is sensitive to pH and redox-conditions within a general acidic setting are good tools to capture differences of topographical situation.

9.3. Darjeeling

Darjeeling tea is a protected designation of origin in the European Union (Council of the European Union 2011a) and only tea grown in Darjeeling should be referred to as 'Darjeeling tea'. As demonstrated in the previous section Darjeeling tea can be discriminated from Assam tea despite very similar geological source rock material. Even more challenging is to discriminate Darjeeling from the adjacent tea producing areas in Nepal. These regions have nearly exactly the same setting of tea cultivation and production parameters including the topographical and geological setting, because the geological domains of the Himalaya orogen strike parallel to the lateral extension of the mountain range (Section 3.1.1). To figure out parameters which could possibly differentiate between East Nepal and Darjeeling the interaction of the tea plants with the their underground has to be studied.

As discussed in the preceding section, the comparably high Al concentrations in tea of Darjeeling suggests a very low pH in the rhizosphere. In Darjeeling, especially in tea gardens practicing an organic cultivation, the *C. sinensis* is probably forced to mobilize nutrients from the mineral fraction of the soil or even the from upper layers of the underlying rocks: The steep topography in combination with high erosion rates and locally very 'young' and shallow soils does not provide rich or stable nutrient reservoirs. Nutrient rich minerals, e.g. muscovites and plagioclase, had been described to be inhabited with bacterial and fungal communities and both are discussed to play an important role for releasing nutrients from the mineral surfaces (Gleeson et al. 2005, 2006; Koele 2012, and references therein). The coarse fraction of the soil, respectively altered upper layers

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of the underlying rocks, is known to be one possible source of nutrients for trees, depending on the degree of weathering of the minerals (Kohler et al. 2000; Heisner et al. 2004, and references therein). Although in Darjeeling compost or other manure is regularly applied, field observations at road cuts showed that tea roots intrude up to more than two meters into solid rock. This supports the assumption that tea in Darjeeling is interacting with the weakly weathered layers of the basement rock to partly cover its nutrient and/or water supply.

Hence, in Darjeeling the ionome could be influenced by the mineral composition of the source rocks of the tea plantation areas. The geological map of Darjeeling displays that tea is mainly grown in two metamorphic zones of the MCTZ, the Grt-Mu-zone and in the St-zone, and the Daling Group (Figure 9.11). Only very few garden sections are located in the Ky-zone due to the very high elevation of this zone. Accordingly, most samples in the Darjeeling data set originate from the Grt-Mu-zone, the St-zone and the transition zone between these two zones (Table 9.6). The Daling zone crops out in the lower elevations of Darjeeling. 'Darjeeling tea' is also produced from plantations covering these lower elevations, but tea from these areas rarely achieves highest qualities. Comparing the number of samples originating of areas with the Daling Group as source rock and the areas covered by tea plantations, the Daling Group is underrepresented in this data set. For developing discrimination functions the groups with very small number of samples have to be excluded. The transition zones are also ignored for this purpose.

Table 9.6.: Number of shoot tip samples and processed tea samples by underlying source rocks in Darjeeling. 'Total N' denotes the number of all samples, including processed tea samples of gardens reaching over more than one source rock type. The second column is the number of samples which originate with high certainty from a single source rock type. Abbreviations: Grt garnet, Mu muscovite, St staurolite, Ky kyanite.

Source rock	total N	samples with high certainty
Alluvium	3	3
Daling Group	4	4
Grt+Mu Gneiss	39	29
St+Grt+Mu Gneiss	28	10
St Gneiss	44	41
Ky Gneiss	1	1

The geochemical composition of the soils for the standard subcomposition, including K and Ca, does apparently not systematically differ between the source rock units (Figure 9.8). On the one hand this could be caused by the comparably homogeneous type

Figure 9.8.: Clr-biplot of soils from Darjeeling for the subcomposition Ca, Co, Cs, K, Mn, Rb, Sr, Y and Zn. Total explained variance is 0.75. Total number of samples is $N=77$. For abbreviations see caption of Table 9.6.

of source rock: The MCTZ consists throughout whole Darjeeling of paragneisses with gradually increasing metamorphic grade from bottom to top (Section 3.1.1). On the other hand it could be a result of a homogenization of soils material through the high erosion rates and re-sedimentation of soil along the slopes.

For the LDA of tea ionome in Darjeeling the two main metamorphic zones, the Grt-Mu-zone and the St-zone, are used as categorical variable. Unfortunately, the samples of the two zones can not be clearly separated by the standard subcomposition. To capture the difference of mineral composition of the two zones the standard subcomposition has to be extended by main elements of the most frequent minerals. The mineral content of the Grt-Mu-zone varies strongly but the main minerals are quartz, biotite, muscovite and garnet. The mineral content of the St-zone shows also considerable variations with the main minerals being quartz, garnet, feldspar and staurolite. The feldspars are in Mottram et al. (2014a) described to be plagioclase (Section 3.1.1). Biotites and muscovites

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belong to the mica group of the sheet silicates. The mineralogical formula for muscovite is $\text{KAl}_2[\text{Si}_3\text{AlO}_{10}](\text{OH},\text{F})_2$ and for biotite $\text{K}(\text{M},\text{Fe}^{2+})_3[\text{Si}_3\text{AlO}_{10}](\text{OH},\text{F})_2$. Hence, both micas include K in between their layers ('sheets') of linked $(\text{SiAl})\text{O}_4$ tetrahedra. Plagioclase is the Ca, Na rich member of the feldspar-group with the formula $\text{Na}[\text{AlSi}_3\text{O}_8]-\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$. Accordingly, K and Ca are added to the element subcomposition. In contrast to other regions most gardens in Darjeeling abstain from the use of K-containing fertilizer products and therefore the concentrations of K in the soils are not significantly influenced by soil management (Section 8.2 and Figure 8.2). The Ca uptake could be altered by recent application of carbonate/dolomite; only for Teesta Valley a recent application could be confirmed. Nevertheless, even for these samples no particularities in the Ca concentration in the ionomes could be detected.

Figure 9.9.: Histogram of shoot tip and processed tea samples displaying the first score of linear discriminant function separating two metamorphic zones of Darjeeling. The element compilation includes Ca and K, and excludes Co, Cs and Rb. Samples are colored by location in Darjeeling District. Only samples with high certainty of source rock are included (Table 9.6). Total number of samples is $N = 70$ (Grt+Mu Gneiss $N = 29$, St Gneiss $N = 41$). For abbreviations see caption of Table 9.6. Clr-scalings for LD1 and misclassifications are listed in Table 9.7.

Table 9.7.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea from to metamorphic zones in Darjeeling. The element compilation includes Ca and K, and excludes Co, Cs and Rb. Table corresponds to Figure E.2). The rows of the misclassification table give the number of samples predicted into respective group.

	Mn	Sr	Zn	Ca	K
LD1	-2.34	-2.69	0.38	6.26	-1.62

	Grt+Mu Gneiss	St Gneiss
Grt+Mu Gneiss	28	1
St Gneiss	5	36

Figure 9.9 displays the results of a LDA with the source rocks as categorical variable and the adjusted element subcomposition including Ca and K. Co, Cs and Rb are omitted, because they have LD1-values close to zero and apparently no discriminating power in this setting. Table 9.7 shows that with the five elements (four ilr-variables) Ca, K, Mn, Sr and Zn the ionome of shoot tips can be discriminated by the metamorphic grade of the parent gneisses. The discrimination can be easily enhanced if one or two trace elements are added to the subcomposition (Figure E.2, Table E.3). The coloring of the histograms indicates that the location of the sampling points has no influence on the discrimination: In both groups tea samples originate from all parts of Darjeeling District, e.g. from the southern parts like Mirik or Kurseong, or from the northern parts like Darjeeling North or Darjeeling West.

The LD1-values are characterized by Ca versus K, Mn and Sr. As expected the Ca weights towards the St-zone. This suggests that in the St-zone Ca is more easily available for the plants than in the Grt-Mu-zone, probably due to the weathering of the plagioclase. On the other side, K seems to be more easily available for the plant in the Grt-Mu-zone, probably due to the high abundance of muscovites/illite/biotite. This coincides with field observations: In certain areas within the Grt-Mu-zone the soil is literally 'glittering' by micas. Interestingly, Sr is contrasting to Ca in the log-linear combination of elements for the discrimination. One possible interpretation is that in the Grt-Mu-zone the lower Ca-availability compared to the shoot tip leads to a higher Sr/Ca ratio during uptake, because the Sr replaces Ca.

Minerals of the garnet group are generally resistant to weathering processes. However, in Darjeeling the C-horizon showed weathered garnets ('red-brown dots') and in the upper layer of the soils no garnets remained. Most probably the garnets have a chemical

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compositions between the Pyrope, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and Almadine, $\text{Fe}_3^{2+}\text{Al}_2\text{Si}_3\text{O}_{12}$, end member. In the parent material of the lower elevations the garnets are not as abundant as in the zone of higher metamorphic grade. There are very few sample sets from the lowest elevations of the Grt-Mu-zone, but the data suggest that subcompositions including Mg could be sensitive to the abundance of small garnet minerals in the low- to middle grade paragneisses of Darjeeling.

In Darjeeling the metamorphic isogrades are nearly horizontally and therefore the increase in metamorphic degree correlates about with the altitude. This can be used to very roughly approximate the altitude of the tea plant's origin within the Grt-Mu-zone and the St-zone. For this purpose the subcompositions Ca, K, Mn, Sr, Y and Zn of all shoot tip data of this zone are projected by means of the LDA scalings from Figure E.2 onto a LD1 axis.

Figure 9.10.: Scatter plot for shoot tip samples of topographical elevation versus LD1 values calculated by the log-linear combination of Table 9.7. Samples are colored by geological source rock of Darjeeling District. The labels denote the sampling points. For abbreviations see caption of Table 9.6.

In Figure 9.10 these 'LD1' values are plotted against the elevation of the sampling points. From this plot four observations can be drawn: 1) It is confirmed that within the Grt-Mu-zone and the St-zone the LD1 values very roughly increase. But estimat-

ing the altitude of the samples by this methods will be subject to a high uncertainty. 2) But, the method is precise enough to find major tectonic offsets in this area: The three samples P14, P20 and P34 are notably 'too deep': All three of these sampling points are located on the southern slope or the northern slope of Darjeeling District. Field observations showed along the topographic 'edges' towards the southern plain or the deep valley of the Teesta River sets of steep dipping normal faults. P14 and P20 could be confirmed by field work that in these locations the source rocks are build up by units of higher grade metamorphic gneisses - presumably huge blocks which had been moved downhill through tectonic events. 3) The sample of the Ky-zone reveals medium LD1-values. The two most prominent minerals of this zone are biotite and kyanite, and accordingly the biotite could serve as a K-source for the plants, similar to the micas of the Grt-Mu-zone. Under this aspect it is logical that with increasing elevation LD1-values - which discriminate between K and Ca rich mineral phases - would again decrease. Additionally, small landslides and intense erosion is a common phenomenon in these very high and steep plantations. Depending on the situation this contributes to a massive downhill transport of fresh material of higher metamorphic degree. 4) The 'AMF' samples growing on Daling Group source rocks show 'too high' LD1 values in relation to their elevation. This data have to be very carefully interpreted because all three samples originate from the same sampling location in the Mullootar Tea Estate, Ambootia Tea Group (Mullootar). It could be a hint for poor K-availability on Daling Group source rocks: The Daling Group consists of amongst other rocks of greenish colored phyllites with a high content of chlorites. Probably one of the main minerals is the chlorite Clinocllore ($[\text{Mg,Fe}^{2+}]_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$). These minerals could be a good source for Mg, Fe and in minor quantities Mn but not for K. However, due to the number of samples the interpretation is highly speculative. The sampling point P15 is mapped to lie within the Daling Group, but the extrapolated contact zone between the Daling Group in the footwall and the Grt-Mu-zone in the hanging wall is not even at 50 m distance. Considering that this is a tectonically very active region and mapping in general is very challenging on these slopes, the plants did not necessarily grow only on Daling Group source rock material.

In summary, the log-linear combination of Table E.3 could serve in Darjeeling as a proxy for the relative mica content in geological source rock. Then again, the content in mica is related to the geological unit, LHS versus MCTZ, and the metamorphic grade of the paragneisses in the MCTZ. Because the metamorphic grade constantly increases with increasing topographical altitude this subcomposition Ca, K, Mn, Sr, Y and Zn may help to very roughly approximate the growing elevation of the tea plant.

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Approximating the altitude will not discriminate between samples from Darjeeling and adjacent gardens in Nepal. But this case study demonstrates how sensitive the ionome of *C. sinensis* can be in terms of mineral composition of the source rock material - or soil parameters which are strongly influenced by this. If the subcompositions of these case studies are going to be extended by even more sensitive trace elements, like Ba or the REE, there is probably a high potential for conducting provenance analysis with a high spatial resolution. First results from a data set with samples from Nepal encourage this hypothesis.

Figure 9.11.: Map of geological units in Darjeeling District with sampling locations of shoot tip samples. DEM downloaded from <http://bhuvan-noeda.nrsc.gov.in>, CartoDEM Ver.3, Toposheet No. G45K, projection WGS 84, UTM Zone 45R, Pseudo Mercator

9.4. Summary

The results of the chapters 6, 7 and 8 allow to estimate for each element how intensely its concentration is altered by a single parameter or a combination of parameter. Additionally, field observations and personal communications help to weight the impact of a parameter. The combination of rating elements and weighting is a qualitative approach to express the robustness of each element concentration in respect to a specific tea cultivation and production: The element list sorted from high suitability for provenance studies to low suitability is Mn, Rb, Cs, Sr, Co, Zn, Cu, Sb, La, Mg, Tl, K, Cd, Pb, Mo, Cr, Al, Y, Ni, Li, Fe, Ca, P, Na, S, Ba, Sc.

In this thesis the tea provenance studies are based on subcompositions which are selected by their general suitability, respectively robustness, and less by their discriminative power in this specific data set. To show the principles of this 'robustness-approach' three case studies are presented with varying categorical variables: 1) Discrimination by countries, 2) discrimination by regions in India and 3) discrimination by geological metamorphic zones in Darjeeling. The six elements with the highest suitability/robustness rating are used as the 'standard' subcomposition: Mn, Rb, Cs, Sr, Co and Zn.

The results of the LDA with the standard element subcomposition exhibit that this subcomposition is suitable to distinguish tea samples roughly by country and by their geological source material. If the standard element subcomposition is extended by elements which capture local specifics the discrimination power between countries can be increased: The results of the LDA with the subcomposition of Mn, Rb, Cs, Sr, Co, Zn, K, P and Li shows that three additional elements K, P and Li help significantly to improve the discrimination between the groups. Only the plants growing on soils with geological parent material containing mafic minerals are still misclassified by this combination of variables.

The samples from Darjeeling and Assam can be discriminated from samples of Nilgiris by the standard subcomposition with roughly a log-linear combination of Co and Zn versus Rb. These results are caused by their 'young' soils in contrast to the deeply weathered soils of Nilgiris: Samples of Nilgiris can be discriminated from samples of Darjeeling and Assam due the contrasting soil geochemistry and the consequential soil management. Tea from Darjeeling can be discriminated from Assam despite very similar soil geochemistry. In both regions the soils display a general acidic setting. In this case elements for which their uptake is sensitive to pH and redox-conditions are good tools to capture the differences of topographical situation. Accordingly, the discriminating log-

linear combination is roughly Al, Zn and Cs versus Ti, Rb, Co and Mn.

In Darjeeling the ionome is probably influenced by the mineral composition of the source rocks of the tea plantation areas. The tea is mainly grown in two metamorphic zones of the MCTZ, the Grt-Mu-zone and in the St-zone, and the Daling Group. The geochemical composition of the soils for the standard subcomposition, including K and Ca, does apparently not systematically differ between the source rock units. To capture the difference of mineral composition of the two zones the standard subcomposition has to be extended by main elements of the most frequent minerals, K and Ca. With the five elements (four ilr-variables) Ca, K, Mn, Sr and Zn the ionome of shoot tips can be discriminated by the metamorphic grade of the parent gneisses. The location of the sampling points in Darjeeling has no influence on the discrimination by metamorphic zone.

The parameter of cultivars does not seem to induce a visible bias on discrimination by regions.

10. Conclusions and Outlook

10.1. Conclusions

A world spanning provenance analysis for tea requires a statistical model which considers that tea is produced in several continents under a broad spectrum of cultivation conditions and manufacturing settings. One task of such a model is to establish methods which will help to reduce the minimal size of the training data sets required for a world wide determination of origin with a high resolution. The necessary size of the data set can be reduced if less elements for the discriminating functions are used and/or if the sample groups are more homogeneous: For example, in a data set all samples are CTC black processed teas produced of only *C. sinensis* var. *assamica* leaf material which was harvested manually with '2 and bud' plucking standard in shaded, organic plantations. This thesis explores the potential of using the ionome, - all the mineral nutrients and trace elements-, of shoot tips of *C. sinensis* for provenance studies and presents methods to determine suitable element subcompositions.

The ionome of tea develops through a combination of parameters of varying impact. One of the main parameters is the geochemical composition of the soils, but also important are climate, topography, soil pH, fertilizing regimes, harvesting method, plucking standard, type of cultivar, season of harvesting, maintenance of the tea bushes, type of plantation, production machines, leaf grade of the processed tea and last but not least, blending. Some of these parameters change between seasons or years, some change within decades and some can be considered as stable. Stable parameters are the geochemical composition of soils (without the fertilizer influence), the topography, and - to some extend - the climate.

Geographical determination is most robust if based on element subcompositions of the ionome which are dominated by the stable parameters. The geographical resolution can be increased either by combining these subcompositions with elements which log-ratios are sensitive to other parameters, or by 'filtering' the data sets prior to the discriminant analysis by with respect to specific parameters.

10. Conclusions and Outlook

The main result of this thesis is the determination of an element subcomposition of the ionome which is dominated by the geochemical composition of the soils and with negligible influence by other parameters. This is achieved by a combination of statistical techniques adjusted for compositional data analysis: Based on the data set used for this thesis the 'standard' subcomposition for geographical discrimination consists of Mn, Rb, Cs, Sr, Co and Zn. To increase the discrimination power between two regions this subcomposition can be modified by adding or removing elements. For example, adding Tl could serve as an indicator for water-logging, Ni and Co for mafic source rock material, or K and Ca as proxy for mineral composition of the underlying basement rocks.

One of the major factors affecting the elemental composition of a leaf sample is the ratio of young (sink) leaves versus mature (source) leaves. The sink/source leaf ratio in processed tea samples results from the harvesting method, plucking standard and the sorting of processed tea material after manufacturing. The average leaf age of a processed tea sample can be estimated by the value of the balanced ratio of [Cu K | Al Ca Mn]. Filtering a data set by this value helps to homogenize the data set in terms of the parameters plucking standard and sorting.

Elements which are typically influenced by fertilizer application are P and K and occasionally S. Ca is potentially influenced by carbonate/dolomite applications to mitigate the pH of the tea soils. Although foliar applications alter other element concentrations in the leaf material as well, effects of foliar sprays containing e.g. Zn or Cu could not be shown in the present data set. In combination with other subcomposition the 'fertilizer' subcomposition can be used to indicate regions where the soil fertility status is very low and therefore intensive fertilizer application is used to meet the plant's requirements.

Processed teas can be contaminated with Cr, Pb, Sb, Sc and Sn by machine abrasion, depending on the type of manufacturing. If the production conditions are unknown these elements should be excluded for provenance studies. In combination with other subcompositions this subcomposition could serve as a proxy for geographical region, because each tea producing region has its 'typical' type of manufacturing.

Generally, the plants' geochemical compositions can also be altered by air-borne or soil-borne adhering particles. Therefore, plant data should always be corrected for adhering particles prior to statistical analysis. Assuming that for tea the geochemical composition of the adhering particles can be approximated by the geochemical composition of the soils of the area the elements Th, Ta, Hf, Zr, U, Nb and Ti should be skipped for provenance analysis. The error of their corrected values is too high for a sound usage of these values.

10.2. Outlook

As mentioned in the introduction, the task of developing a holistic model for world-wide provenance studies on tea is not solved by this thesis. This thesis proposes merely statistical approaches for several of the components of such a model.

Many components of an holistic model are not discussed in this thesis. The most important one is the blending of tea. The blending can change the elemental composition of processed tea samples up to an extend that it is impossible to conduct provenance analysis. At the best, blending will give a 'blend signature' which helps to distinguish - prior to any other statistical analysis - blends from tea of several regions from blends of tea originating from small, distinct areas. First data point towards such a 'blend signature', but investigating the effect of blending on the resolution of provenance studies is of uttermost importance for future projects.

In order to develop further components for a holistic model the data set has to be increased. Interesting data sets would be samples of the same region, but with contrasting cultivation techniques, sample sets of the same cultivar growing in contrasting climate conditions, samples sets where only the harvesting method differs, and generally sample sets from China, Indonesia, Sri Lanka, Kenia, Vietnam and Japan. A bigger and more diverse data set will also alter the results of this thesis.

One part of developing the holistic model will be to quantify the robustness and suitability of elements or element subcompositions in respect to certain parameters. This requires a bigger data set for the discussion of further parameters and a more complex statistical approach, e.g. through intercalating the analysis of several parameters. Several of the proposed methods have to be refined, like introducing techniques which incorporate the analytical errors of each data point and meet the special requirements of compositional data.

Last but not least, future projects should include more variables. For example, the existing data set provides also lanthanide data which are not discussed in this thesis but showed encouraging results for provenance studies. The data set could also be combined with isotopic data and/or data of organic components. A better understanding of the plant/soil interaction would help to interpret the variables in terms of their impact for provenance studies. Especially interesting will be to explore the role of trace elements and elements which are in their chemical characteristics analogous to nutrients.

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A. Tea and Sampling Areas

Figure A.1.: Outcrop along recently renewed street inside Nagri Farm of saprolitic schist of Main Central Thrust Zone unit, garnet-muscovite zone.
N 26°55'37, E 88°13'05, WGS 84

Figure A.2.: Hand specimen (length ~10 cm) of the Main Central Thrust Zone unit, garnet-muscovite zone, close to the footwall of the garnet-muscovite zone. Small staurolite needles are growing parallel to the foliation plane of the schist.
N 27°06'05, E 88°14'44, WGS 84

A. Tea and Sampling Areas

Figure A.3.: Small boulder of the Main Central Thrust Zone unit, staurolite zone, with crinoidal matrix. Boulder is placed in the structurally upper level of garnet-muscovite zone.

N 26°53'25, E 88°17'91, WGS 84

Figure A.4.: Huge boulder of the Main Central Thrust Zone unit, staurolite zone, placed in the close towards the hanging wall of the garnet-muscovite zone. See plant leaves for scale. Micaceous layers are strongly foliated while quartz-feldspathic layers are sheared into thin, undulating bands or boudin-like lenses.

N 26°51'56, E 88°16'23, WGS 84

Figure A.5.: River boulder of the Main Central Thrust Zone unit, kyanite zone.

N 27°02'50, E 88°10'25, WGS 84

Figure A.6.: Hand specimen (length ~24 cm) of Main Central Thrust Zone unit, kyanite zone. In the right upper corner of the specimen is a leucosome consisting of $Qz \pm Ky \pm Grt \pm St$ and accessories.

N 26°51'56, E 88°16'23, WGS 84

Table A.1.: List of tea estates in Darjeeling registered with the Tea Board of India to form the geographical indication 'Darjeeling' as a protected entity.

Aloobari Tea Estate	Namring Tea Estate (& Namring Upper)
Ambiok(Hilton) Tea Estate	Nagri Farm Tea Estate (Makurjung)
Ambootia Tea Estate	Narbada Majhua Tea Estate
Arya Tea Estate (Sidrabong)	North Tukvar Tea Estate
Avongrove Tea Estate	Nurbong Tea Estate
Badamtam Tea Estate	Oaks Tea Estate
Balasun Tea Estate	Okayti Tea Estate
Bannockburn Tea Estate	Orange Valley Tea Estate
Barnesbeg Tea Estate (North Tukvar)	Pandam Tea Estate
Castleton Tea Estate	Peshok Tea Estate
Chamong Tea Estate	Phoobsering Tea Estate
Chongtong Tea Estate (Sirisi)	Phuguri Tea Estate
Dhajea Tea Estate	Poobong Tea Estate
Dilaram Tea Estate	Pussimbing Tea Estate (Minzoo)
Dooteriah Tea Estate	Rangaroon Tea Estate
Edenvale Tea Estate (Maharani)	Ringtong Tea Estate
Gayabari Tea Estate (Millikthong)	Risheehat Tea Estate
Giddhapahar Tea Estate	Rohini Tea Estate
Gielle Tea Estate	Runglee-Rungliot Tea Estate
Ging Tea Estate	Rungmook Tea Estate (Cedars)
Glenburn Tea Estate	Samabeong Tea Estate
Goomtee Tea Estate	Seepoydhoorah Tea Estate (Chamling)
Gopaldhara Tea Estate	Seeyok Tea Estate (Spring Valley)
Happy Valley Tea Estate	Selim Hill Tea Estate
Jogamaya Tea Estate	Selimbong Tea Estate (Rongbong)
Jungapana Tea Estate (Jungapana Upper)	Singbulli Tea Estate
Kalej Valley Tea Estate	Singell Tea Estate
Kanchaan View Tea Estate (Rungeet)	Singtam Tea Estate
Kumai Tea Estate (Snow View)	Sivitar Tea Estate
Lingia Tea Estate	Soom Tea Estate
Liza Hill Tea Estate	Sourennee Tea Estate
Longview Tea Estate (High Lands)	Springside Tea Estate
Lopchu Tea Estate	Steinthal Tea Estate
Mahalderam Tea Estate	Sungma Tea Estate
Makaibari Tea Estate	Teesta Valley Tea Estate
Margaret's Hope Tea Estate	Thurbo Tea Estate
Marybong Tea Estate	Tindharia Tea Estate
Mim Tea Estate	Tukvar Tea Estate (Puttabong)
Mission Hill Tea Estate	Tukdah Tea Estate
Mohan Majhua Tea Estate	Tumsong Tea Estate
Moonteviot Tea Estate	Turzum Tea Estate
Moondakotee Tea Estate	Upper Fagu Tea Estate
Mullootar Tea Estate	Vah Tukvar Tea Estate (Shree Dwarika)
Nagari Tea Estate	

A. Tea and Sampling Areas

Table A.2.: List of leave size classes and the respective grades of orthodox black tea

Class	Grade	Nomenclature
Whole leaf	FTGFOP	Fine, Tippy golden flowery orange pekoe
	TGFOP	Tippy golden flowery orange pekoe
	TGFOP 1	Tippy golden flowery orange pekoe one
	GFOP	Golden flowery orange pekoe
	FOP	Flowery orange pekoe
	OP	Orange pekoe
Broken	GFBOP	Golden flowery broken orange pekoe
	FBOP	Flowery broken orange pekoe
	GBOP	Golden broken orange pekoe
	BOP 1	Broken orange pekoe one
	BPS	Broken pekoe souchong
Fannings	GOF	Golden orange fannings
	FOF	Flowery orange fannings
	BOPF	Broken orange pekoe fannings
	OF	Orange fannings
Dust	OPD	Orthodox pekoe dust
	OD	Orthodox dust
	OCD	Orthodox churamoni dust
	FD	Fine dust

Figure A.7.: Typically weathered outcrop along a street of amphibolite grade gneisses (Kangchenjunga Gneiss (GHS) unit). The weathered aspect might trick the eye into describing the rock as "Augengneiss", but if the weathered cover is removed the outcrop looks like Figure 3.12.
N 27°00'55, E 88°15'08, WGS 84

Figure A.8.: Boulder of amphibolite grade gneiss (Kangchenjunga Gneiss (GHS) unit) in a stream, 65 m distance to top of the ridge. Darkish mineral right above the hammer is a fist-sized garnet.
N 27°01'33, E 88°15'45, WGS 84

Figure A.9.: Schematic map (not in scale) of Upper Assam, India, from publication Karak et al. (2015a). The location of soil samples for the description of the tea soils in Assam are indicated by the sampling sites in this map.

A. Tea and Sampling Areas

Figure A.10.: Map of tea growing regions and their geological setting in Brazil. Geological map: MM Perrotta et al. (2005). Mapa geológico do Estado de São Paulo, escala 1: 750.000. São Paulo: CPRM. Tea estates redrawn after satellite images 2017 (Google satellite). Projection WGS 84, UTM Zone 23J, Pseudo Mercator.

B. Sample Preparation and Analysis

B.1. Digestion Protocol

B.2. Protocol for Tea Brewing

1. 100 mL of water, either distilled or tap water, boiled in a Perfluoroalkoxy (PFA) bottle are poured in a 100 mL Teflon® cup containing 2 g of tea.
2. The tea is brewed for 5 min in the cup.
3. The tea is filtered with a Teflon filter and split into two 50 mL units: one is used for pH-measurements and after this the sample is dried in order to determine the amount of dissolved organic. The other 50 mL are stored in Polyethylen (PE) bottles and 100 µg of IS is added. The left over leaf material is dried and weighed in order to determine the weight of the organic residue after cooking.

B.3. Protocol for Plant Digestion

newest version by: Benedikt Sauer, Hans Ruppert, Solveig Pospiech, Aug. 2014

1. 400 mg to 500 mg (best is maximum 450 mg) of powdered tea plant material are weighed into the Teflon® cups of PicoTrace digestion equipment. Minimum one cup is used for an international plant standard sample like BCR-129, NJV 94-5 or GBW 10052 and minimum one cup is reserved for the *blind*, where no sample material is weighed in.
2. Pre-reaction: At room temperature 4 mL of concentrated HNO₃ are added into every cup and let react for several hours (e.g. over night). Then the cups are heated up to 30 °C within 5–10 h (depending on the reactivity of the powder), kept at this temperature for 12 h, then further heated up to 50 °C within 5–10 h and kept at the temperature for another 12 h.
If the reaction slowed down after these steps 0.5 mL of conc. HF and 3 mL of conc.

B. Sample Preparation and Analysis

HClO₄ are added. Then the cups are further heated up to 100 °C within 2 h and kept at this temperature 4–5 h until all reactions are ceased.

3. Pressure phase I: Ontop the cups pressure plates are mounted. From the temperature of 100 °C the cups are heated within 3 h up to 150 °C and then kept at this temperature for another 15 h.
4. Vaporization of acids: After cooling down the pressure plates are unmounted and the acids in the cups are vaporized by heating up the cups within 12 h to 180 °C, keeping temperature for 24 h and then letting cool down.
5. Pressure phase II: By now all acids should be vaporized and the residue in the cups should be dry. In every cup 0.5 mL of conc. HNO₃ and 10 mL ultraclean H₂O are added. For better dissolution the cups are heated up to 150 °C within 1 h and kept at this temperature for 2 h. After cooling 50 µL of IS is added to every sample.
6. Solution transfer: The clear solution is transferred into a 25 mL narrow-necked volumetric flask, filled up to 25 mL with ultraclean water and then homogenised. 50 mL PE-bottles are pre-conditioned by a few mL of the digestion solution and then discarded. The rest of the solution is transferred from the volumetric flask into the sample bottles.

B.4. Protocol for Soil Digestion

newest version by: Benedikt Sauer, 2011

1. 100–120 mg of powered soil material are weighed into the Teflon® cups of Pico-Trace digestion equipment. One cup is used for the rock standard TW-45 and at least one cup is reserved for the *blind* solution, where no sample material is weighed in.
2. Pre-reaction: At room temperature 2 mL of conc. HNO₃ are added into every cup and let react for several hours. Then 3 mL of conc. HF and 3 mL of conc. HClO₄ are added.
3. Pressure phase I: Ontop the cups pressure plates are mounted and bolt down. Within 3 h the cups are heated up to 150 °C and then kept at this temperature for another 5 h. Then they are cooled down.

4. Vaporization of acids: The pressure plates are unmounted. The acids in the cups are vaporized by heating up the cups within 6 h to 180 °C, keeping that temperature for 10 h and then they are cooled down.
5. Pressure phase II: By now all acids should be vaporized and the residues in the cups should be dry. In every cup 2 mL of conc. HNO₃, 0.6 mL conc. HCl and 10 mL ultraclean H₂O are added. For a better dissolution the cups are heated up to 150 °C within 1 h and kept at this temperature for 2 h. After cooling down 200 µL of IS are added to every sample.
6. Solution transfer: The clear and precipitation free solution are transferred into a 100 mL narrow-necked volumetric flask, filled up to 100 mL with ultraclean water and then homogenised. 100 mL PE-bottles are pre-conditioned by a few mL of the digestion solution and the discarded. The rest of the solution is transferred from the volumetric flask into the sample bottles.

B.5. Calibration Solutions

Table B.1.: Composition of Internal Standard for ICP-MS analysis (concentration given in µg/L [ppb])

Element	mass	Internal Standard until Aug'13	Internal Standard after Aug'13
Be	9	-	100
Ge	73	50	-
Rh	103	10	20
In	115	10	10
Re	185	20	10

B. Sample Preparation and Analysis

Table B.2.: Concentration of 100 %-calibration solution for ICP-MS analysis (concentration given in mg/L [ppm])

Element (mg/L [ppm])	calibration sol. 100 % (2 % Vol. conc. HNO ₃)
Al	1
As	0.05
B	1
Ba	0.5
Be	0.02
Bi	0.005
Ca	0.5
Cd	0.01
Ce	0.05
Co	0.05
Cr	0.2
Cs	0.01
Cu	0.1
Dy	0.004
Er	0.004
Eu	0.0025
Fe	1
Ga	0.2
Gd	0.005
Hf	0.02
Ho	0.002
K	1
La	0.05
Li	0.2
Lu	0.001
Mg	1
Mn	0.5
Mo	0.02
Na	1
Nb	0.1
Nd	0.025
Ni	0.2
Pb	0.05
Pr	0.01
Rb	0.2
Sb	0.02
Sc	0.025
Se	0.01
Sm	0.005
Sn	0.02
Sr	0.5
Ta	0.01
Tb	0.002
Th	0.025
Ti	1
Tl	0.005
Tm	0.001
U	0.005
V	0.2
W	0.02
Y	0.025
Yb	0.005
Zn	0.4
Zr	0.2

Table B.3.: Concentration of 100 %-calibration solution for soil samples and tea samples for ICP-OES analysis, used until May 2015 (concentration given in mg/L [ppm])

Element (mg/L [ppm])	soil calibration sol. 100 % (2 % Vol. conc. HNO ₃ , 0.5 % Vol. 6N HCl)	plant calibration sol. 100 % (2 % Vol. conc. HNO ₃)
Al	500	20
Ba	10	5
Be	0.1	0.1
Ca	200	400
Cd	0.2	0.1
Ce	1	
Co	1	0.1
Cr	2	0.1
Cu	1	0.5
Fe	400	10
Ga	2	
K	200	600
La	1	
Li	2	
Mg	200	100
Mn	10	6
Mo	1	1
Na	100	50
Nb	0.5	
Ni	2	1
P	5	250
Pb	2	1
S	50	150
Sc	1	0.1
Sn	0.5	
Sr	5	4
Ti	25	1
V	2	
Zn	2	10
Zr	2.5	

B. Sample Preparation and Analysis

Table B.4.: Concentration of 100 %-calibration solution for soil samples and tea samples for ICP-OES analysis, used from June 2015 onwards (concentration given in mg/L [ppm])

Element (mg/L [ppm])	soil calibration sol. 100 % (2 % Vol. conc. HNO ₃ , 0.5 % Vol. 6N HCl)	plant calibration sol. 100 % (2 % Vol. conc. HNO ₃)
Al	200	20
Ba	10	5
Be	0.2	0.1
Ca	100	400
Cd	0.1	2
Ce	1	
Co	0.25	0.1
Cr	0.5	0.1
Cu	0.5	1
Fe	100	50
Ga	0.5	
K	100	1000
La	1	
Li	0.5	
Mg	50	100
Mn	10	5
Mo	0.25	0.25
Na	25	20
Nb	0.5	
Ni	0.5	0.25
P	5	250
Pb	0.5	0.25
S	10	100
Sc	0.25	0.1
Sn	0.25	
Sr	2.5	2
Ti	25	2
V	1	
Zn	0.5	2.5
Zr	2	

Table B.5.: Concentration of maximal calibration solution for soil samples and tea samples for ICP-OES analysis, used from June 2015 onwards (concentration given in mg/L [ppm]). This calibration solution is included into the calibration curve if samples show concentrations significantly above the 100%-calibration point

Element (mg/L [ppm])	soil calibration sol. Max (2 % Vol. conc. HNO ₃ , 0.5 % Vol. 6N HCl)	plant calibration sol. Max (2 % Vol. conc. HNO ₃)
Al		200
Ca	500	1000
Cr		1
Cu	2	
Fe		100
Mg	200	400
Mn		50
Mo		1
Na		200
Ni		1
Pb	2.5	1
S	50	
Sr		4
Ti		10
Zn	5	20

Table B.6.: Selected element datum by for each series (date of digestion) from ICP-MS and ICP-OES.

Date.digestion	Type	Al	Ba	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy
2011-07-01	Plant	Al.396.152	Ba.233.527	Ca.315.887	Cd114	Ce140	Co59	Cr.267.716	Cs133	Cu.327.395	Dy163
2011-08-01	Rock	Al.308.215	Ba.233.527	Ca.315.887	Cd114	Ce.413.765	Co.228.615	Cr.267.716	Cs133	Cu.327.395	Dy163
2011-08-30	Plant	Al.396.152	Ba.233.527	Ca.315.887	Cd114	Ce140	Co59	Cr.267.716	Cs133	Cu.324.752	Dy163
2011-09-01	Plant	Al.396.152	Ba.233.527	Ca.315.887	Cd114	Ce140	Co59	Cr.267.716	Cs133	Cu.327.395	Dy163
2014-07-24	Plant	Al.308.215	Ba.233.527	Ca.315.887	Cd114	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2014-08-03	Rock	Al.308.215	Ba.455.403	Ca.315.887	Cd114	Ce140	Co59	Cr.267.716	Cs133	Cu.324.752	Dy163
2014-09-12	Soil	Al.308.215	Ba.233.527	Ca.422.673	Cd111	Ce.446.021	Co59	Cr.267.716	Cs133	Cu.327.395	Dy163
2014-11-01	Rock	Al.308.215	Ba.233.527	Ca.183.944	Cd114	Ce140	Co.230.786	Cr.205.560	Cs133	Cu.324.754	Dy163
2014-12-01	Plant	Al.396.152	Ba.493.408.rad	Ca.317.933.rad	Cd.214.439	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2015-02-01	Rock	Al.308.215	Ba.233.527	Ca.183.944	Cd114	Ce140	Co.230.786	Cr.205.560	Cs133	Cu.327.395	Dy163
2015-07-09	Plant	Al.396.152	Ba.455.403	Ca.422.673.rad	Cd.214.439	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2016-01-27	Rock	Al.308.215	Ba.233.527	Ca.422.673	Cd114	Ce.446.021	Co.230.786	Cr.206.158	Cs133	Cu.327.395	Dy163
2016-05-15	Plant	Al.396.152	Ba137	Ca.317.933	Cd114	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2016-08-05	Plant	Al.396.152	Ba135	Ca.317.933	Cd111	Ce140	Co.230.786	Cr052	Cs133	Cu.327.395	Dy163
2016-10-05	Plant	Al.396.152	Ba.455.403.rad	Ca.317.933	Cd0114	Ce140	Co.230.786	Cr.205.560	Cs133	Cu.327.395	Dy163
2017-03-07	Plant	Al.396.152	Ba.455.403	Ca.317.933	Cd111	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2017-04-07	Plant	Al.396.152	Ba137	Ca.317.933.rad	Cd0114	Ce140	Co.230.786	Cr.267.716	Cs133	Cu.327.395	Dy163
2017-04-14	Plant	Al.396.152	Ba.493.408.rad	Ca.317.933.rad	Cd111	Ce140	Co.230.786	Cr.267.716	Cs133	Cu065	Dy163

Table B.7.: Selected element datum, continued from table B.6

Date.digestion	Er	Eu	Fe	Gd	Hf	Ho	K	La	Li	Lu	Mg	Mn
2011-07-01	Er166	Eu153	Fe.259.940	Gd157	Hf177	Ho165	K.766.491	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2011-08-01	Er166	Eu151	Fe.238.863	Gd157	Hf177	Ho165	K.766.491	La.408.671	Li.670.783	Lu175	Mg.279.078	Mn.257.610
2011-08-30	Er166	Eu153	Fe.259.940	Gd157	Hf177	Ho165	K.766.491	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2011-09-01	Er166	Eu151	Fe.259.940	Gd157	Hf177	Ho165	K.766.491	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2014-07-24	Er166	Eu151	Fe.259.940	Gd157	Hf178	Ho165	K.404.721	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2014-08-03	Er166	Eu151	Fe.238.204	Gd158	Hf178	Ho165	K.404.721	La.408.671	Li7	Lu175	Mg.279.078	Mn.260.568
2014-09-12	Er166	Eu151	Fe.234.350	Gd157	Hf178	Ho165	K.769.897	La.333.749	Li.670.783	Lu175	Mg.279.553	Mn55
2014-11-01	Er166	Eu151	Fe.234.350	Gd158	Hf178	Ho165	K.769.897	La.333.749	Li7	Lu175	Mg.279.078	Mn.257.610
2014-12-01	Er166	Eu151	Fe.259.940	Gd157	Hf178	Ho165	K.766.491.rad	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2015-02-01	Er166	Eu153	Fe.259.940	Gd158	Hf178	Ho165	K.769.897	La.333.749	Li7	Lu175	Mg.279.078.rad	Mn.257.610
2015-07-09	Er166	Eu151	Fe.259.940	Gd157	Hf178	Ho165	K.766.491.rad	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2016-01-27	Er166	Eu151	Fe.259.940	Gd157	Hf178	Ho165	K.769.897	La.333.749	Li.670.783	Lu175	Mg.285.213	Mn.257.610
2016-05-15	Er166	Eu151	Fe.259.940	Gd157	Hf178	Ho165	K.766.491.rad	La139	Li7	Lu175	Mg.285.213	Mn.257.610
2016-08-05	Er166	Eu153	Fe.259.940	Gd157	Hf178	Ho165	K.766.491.rad	La.408.671	Li.670.783	Lu175	Mg.285.213	Mn055
2016-10-05	Er166	Eu153	Fe.259.940	Gd157	Hf180	Ho165	K.766.491.rad	La.408.671	Li.670.783	Lu175	Mg.285.213	Mn.279.482
2017-03-07	Er166	Eu153	Fe.259.940	Gd157	Hf178	Ho165	K.766.491.rad	La.408.671	Li.670.783	Lu175	Mg.285.213	Mn.257.610
2017-04-07	Er166	Eu151	Fe.259.940	Gd157	Hf180	Ho165	K.766.491.rad	La.408.671	Li.670.783	Lu175	Mg.285.213	Mn.257.610
2017-04-14	Er166	Eu151	Fe.259.940	Gd157	Hf180	Ho165	K.766.491.rad	La.408.671	Li.670.783	Lu175	Mg.285.213	Mn.257.610

Table B.8.: Selected element datum, continued from table B.6

Date.digestion	Mo	Na	Nb	Nd	Ni	P	Pb	Pr	Rb	S	Sb	Sc
2011-07-01	Mo98	Na23	Nb93	Nd143	Ni60	P.178.222	Pb208	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2011-08-01	Mo95	Na.589.592	Nb.309.417	Nd143	Ni.231.604	P.214.914	Pb208	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2011-08-30	Mo98	Na.589.592	Nb93	Nd143	Ni60	P.178.222	Pb208	Pr141	Rb85	S.180.669	Sb121	Sc.361.383
2011-09-01	Mo98	Na23	Nb93	Nd143	Ni.231.604	P.178.222	Pb208	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2014-07-24	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.231.604	P.178.222	Pb208	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2014-08-03	Mo98	Na.330.237	Nb93	Nd143	Ni.231.604	P.178.222	Pb.220.353	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2014-09-12	Mo98	Na.588.995	Nb93	Nd146	Ni60	P.213.618	Pb208	Pr141	Rb85	S.180.669	Sb121	Sc45
2014-11-01	Mo98	Na.588.995.rad	Nb93	Nd143	Ni.216.555	P.214.914	Pb208	Pr141	Rb85	S.180.669	Sb121	Sc45
2014-12-01	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.231.604	P.178.222	Pb208	Pr141	Rb85	S.181.972		Sc.361.383
2015-02-01	Mo98	Na.588.995.rad	Nb93	Nd143	Ni.216.555	P.214.914	Pb208	Pr141	Rb85	S.180.669	Sb121	Sc.335.372
2015-07-09	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.231.604	P.178.222	Pb.220.353	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2016-01-27	Mo98	Na.588.995.rad	Nb.309.417	Nd146	Ni.221.648	P.213.618	Pb.220.353	Pr141	Rb85	S.182.562	Sb121	Sc.335.372
2016-05-15	Mo98	Na.588.995.rad	Nb93	Nd146	Ni62	P.178.222	Pb208	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2016-08-05	Mo98	Na.588.995.rad	Nb93	Nd146	Ni060	P.178.222	Pb.220.353	Pr141	Rb85	S.181.972	Sb121	Sc.335.372
2016-10-05	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.231.604	P.178.222	Pb206	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2017-03-07	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.216.555	P.178.222	Pb206	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2017-04-07	Mo98	Na.588.995.rad	Nb93	Nd146	Ni.216.555	P.178.222	Pb206	Pr141	Rb85	S.181.972	Sb121	Sc.361.383
2017-04-14	Mo98	Na.588.995.rad	Nb93	Nd144	Ni060	P.178.222	Pb.220.353	Pr141	Rb85	S.181.972	Sb121	Sc.361.383

Table B.9.: Selected element datum, continued from table B.6

Date.digestion	Sm	Sr	Ta	Tb	Th	Ti	Tl	Tm	U	Y	Yb	Zn	Zr
2011-07-01	Sm147	Sr.407.771	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb173	Zn.213.857	Zr90
2011-08-01	Sm147	Sr.421.552	Ta181	Tb159	Th232	Ti.334.903	Tl205	Tm169	U238	Y89	Yb173	Zn.213.857	Zr.343.823
2011-08-30	Sm147	Sr.407.771	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb173	Zn.213.857	Zr90
2011-09-01	Sm147	Sr.407.771	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb173	Zn.213.857	Zr90
2014-07-24	Sm152	Sr.232.235	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2014-08-03	Sm147	Sr.421.552	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.206.200	Zr.343.823
2014-09-12	Sm152	Sr.460.733	Ta181	Tb159	Th232	Ti49	Tl205	Tm169	U238	Y89	Yb174	Zn.330.258	Zr.343.823
2014-11-01	Sm147	Sr.460.733	Ta181	Tb159	Th232	Ti.334.941	Tl205	Tm169	U238	Y89	Yb174	Zn.213.857	Zr.343.823
2014-12-01	Sm147	Sr88	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2015-02-01	Sm147	Sr.460.733	Ta181	Tb159	Th232	Ti.368.520		Tm169	U238	Y89	Yb174	Zn.213.857	Zr.343.823
2015-07-09	Sm147	Sr.421.552.rad	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2016-01-27	Sm147	Sr.460.733	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb174	Zn.213.857	Zr.343.823
2016-05-15	Sm147	Sr.421.552.rad	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2016-08-05	Sm147	Sr.421.552.rad	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2016-10-05	Sm147	Sr.421.552.rad	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2017-03-07	Sm152	Sr.421.552.rad	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2017-04-07	Sm147	Sr88	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90
2017-04-14	Sm147	Sr88	Ta181	Tb159	Th232	Ti.336.122	Tl205	Tm169	U238	Y89	Yb172	Zn.213.857	Zr90

B.6. Reference Samples

Table B.10.: Certified values of the international and in-house reference materials

	BCR- 129 hay powder	GBW 10052 Tea	NCS DC 73349 bush twigs and leaves	NJV 94-5 wood fuel	Clayey Shale 59 Wissenbacher Tonschiefer
Al	112	-	2000	260	81500
As	-	0.27	1.25	0.80	8.5
Ba	-	41	18	-	380
B	-	14.1	38.0	-	-
Be	-	0.025	0.051	-	3
Bi	-	0.040	0.023	-	0.27
Ca	6400	12100	16800	3500	25400
Cd	-	0.076	0.380	0.270	0.23
Ce	-	0.81	2.20	-	81
Co	0.12	0.30	0.41	-	18
Cr	2.50	0.92	2.60	0.80	105
Cs	-	0.58	0.27	-	7.8
Cu	10.0	24.0	6.6	2.2	35
Dy	-	0.065	0.130	-	5.5
Er	-	0.037	-	-	3.1
Eu	-	0.022	0.039	-	1.2
Fe	114	322	1070	70	45000
Ga	-	-	-	-	21
Gd	-	0.076	0.190	-	5.9
Ge	-	0.015	-	-	-
Hf	-	-	0.15	-	4.7
Ho	-	0.013	0.033	-	1.1
K	33800	15500	9200	900	30300
La	-	0.54	1.25	-	40
Li	-	0.52	2.60	-	48
Lu	-	0.0062	0.0110	-	0.44
Mg	1450	2200	4800	300	23500
Mn	72	1170	61	210	550
Mo	1.00	0.11	0.28	-	0.48
Na	3490	100	19600	40	6600
Nb	-	0.05	-	-	16
Nd	-	0.35	1.00	-	38
Ni	-	5.4	1.7	-	72
P	2360	2800	1000	210	393
Pb	-	1.60	47.00	0.68	38
Pr	-	0.093	0.240	-	9.3
Rb	50.0	89.0	4.5	-	155
S	3160	4200	7300	180	4000
Sb	-	0.052	0.095	-	1
Sc	0.017	0.070	0.320	-	14
Se	0.025	0.100	0.120	-	0.7
Sm	-	0.066	0.190	-	6.9
Sn	-	0.17	0.27	-	3.3
Sr	22.1	36.0	246.0	-	90
Ta	-	-	-	-	2
Tb	-	0.0114	0.0250	-	0.85
Th	-	0.079	0.360	-	13
Ti	3.8	21.0	95.0	2.4	4300
Tl	-	0.057	-	-	0.77
Tm	-	0.0059	-	-	0.5
U	-	0.047	0.120	-	3.3
V	-	0.6	2.4	-	105
W	-	-	0.06	-	2
Y	-	0.52	0.68	-	31
Yb	-	0.038	0.063	-	2.9
Zn	32.1	35.0	55.0	38.0	115
Zr	-	-	-	-	180

Table B.11.: Results (in ppm) of references samples of the selected element analysis of ICP-MS and ICP-OES. Please note: This table includes all measured elements, including the elements of poor analytical quality.

Type	Species	ProjNr	Date.digestion	Al	As	B	Ba	Bi	Ca	Cd	Ce	Co
Plant	NJV 94-5 (wood fuel)	SOL-njv1_mt1	2011-07-01	219	0.505	<LOD	28.5	0.00463	3060	0.238	0.0585	0.0619
Plant	NJV 94-5 (wood fuel)	SOL-njv2_mt1	2011-07-01	252	0.714	<LOD	28.8	0.00469	3070	0.223	0.0529	0.0629
Plant	BCR- 129 (hay powder)	SOL-bcr_tee1	2011-08-30	118	0.705	284	11.4	0.00156	6310	0.0955	0.191	0.0699
Plant	NJV 94-5 (wood fuel)	SOL-njv_tee1	2011-08-30	256	0.807	904	31.2	0.00601	3270	0.241	0.0498	0.0644
Plant	BCR- 129 (hay powder)	SOL-bcr.bl1	2011-09-01	128	0.0618	434	11.4	0.000726	6200	0.0983	0.142	0.0797
Plant	NJV 94-5 (wood fuel)	SOL-njv1.bl1	2011-09-01	236	1.24	<LOD	28.8	0.00567	3070	0.192	0.0392	0.0591
Plant	NJV 94-5 (wood fuel)	SOL-njv2.bl1	2011-09-01	237	0.742	116	30.4	0.00538	3210	0.206	0.0415	0.0631
Plant	GBW 10052 (Tea)	SOL-gbw1_mt2	2012-01-10	1500	0.238	103	39	0.0308	5880	0.0757	0.811	0.28
Plant	GBW 10052 (Tea)	SOL-gbw3_mt2	2012-01-10	1570	0.256	76.7	37.6	0.00339	6030	0.0729	0.781	0.272
Plant	NJV 94-5 (wood fuel)	SOL-njv_mt2	2012-01-10	241	0.862	30.2	30.1	0.00531	1530	0.238	0.0408	0.0682
Plant	GBW 10052 (Tea)	SOL-gbw_tee2	2014-07-24	1660	0.288	16.8	38.8	0.0386	11200	0.0769	0.95	0.267
Plant	GBW 10052 (Tea)	SOL-gbw_tee3	2014-12-01	1780	0.308	15.2	41.8	0.0342	12600	0.06	0.895	0.262
Plant	GBW 10052 (Tea)	SOL-gbw1_tee4	2015-07-09	1760	0.59	16	38.9	0.0376	11300	0.0624	0.962	0.251
Plant	GBW 10052 (Tea)	SOL-gbw2_tee4	2015-07-09	1740	0.564	15.4	39.5	0.0359	11400	0.0659	0.871	0.281
Plant	GBW 10052 (Tea)	SOL-gbw_mt3	2016-05-15	1730	0.27	2.48	40.4	0.0314	12100	0.0757	0.839	0.279
Plant	GBW 10052 (Tea)	SOL-gbw_mt4	2016-08-05	1770	0.274	4.62	40.2	0.0268	11800	0.0722	0.805	0.279
Plant	GBW 10052 (Tea)	SOL-gbw1_tee5	2016-10-05	1720	0.31	7.37	39.7	0.0389	11600	0.101	1.3	0.245
Plant	GBW 10052 (Tea)	SOL-gbw2_tee5	2016-10-05	1710	0.311	8.02	40.8	0.0302	11700	0.0779	0.88	0.273
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee5	2016-10-05	1990	1.18	8.67	16.9	0.0127	15800	0.718	2.31	0.367
Plant	GBW 10052 (Tea)	SOL-gbw_tee6	2017-03-07	1720	0.281	4.71	39	0.0243	11700	0.0608	0.774	0.234
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee6	2017-03-07	2110	1.17	6.93	16.7	0.0136	16800	0.713	2.51	0.367
Plant	GBW 10052 (Tea)	SOL-gbw_tee7	2017-04-07	1740	0.312	8.57	38.4	0.0305	11600	0.0778	0.844	0.228
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee7	2017-04-07	2150	1.38	6.5	17.5	0.0125	17600	0.677	2.02	0.387
Plant	GBW 10052 (Tea)	SOL-gbw_mt5	2017-04-14	1760	0.319	6.51	41	0.0288	11900	0.0791	0.811	0.233
Rock	Clayey Shale 59	SOL-tw_bd1	2011-08-01	78900	6.6	<LOD	375	0.351	25400	0.199	78.2	22.5
Rock	Clayey Shale 45	SOL-tw_bd2	2014-08-03	81900	7.05	<LOD	378	0.283	26100	0.204	93	17.4
Rock	Clayey Shale 45	SOL-tw_bd3	2014-11-01	82000	7.69	<LOD	371	0.25	26500	0.157	82.7	18.1
Rock	Clayey Shale 45	SOL-tw_bd4	2015-02-01	82200	7.71	<LOD	371	0.244	26500	0.165	84.4	18.4
Rock	Clayey Shale 45	SOL-tw_bd5	2016-01-27	81200	10.6	<LOD	360	0.25	26500	0.178	84.8	17

Table B.12.: Reference samples, continued from table B.11

ProjNr	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Hf	Ho	K	La	Li	Lu
SOL-njv1_mt1	0.419	0.0605	1.64	0.00313	0.00161	<LOD	49.2	3.11	0.00467	0.00423	0.00063	943	0.051	0.0224	0.000257
SOL-njv2_mt1	0.554	0.0412	1.96	0.00263	0.00138	<LOD	50.3	2.67	0.00385	0.00385	0.000503	975	0.0415	0.0248	0.000201
SOL-bcr_tee1	2.31	0.0802	9.39	0.00854	0.00328	0.002	113	5.57	0.0125	0.00685	0.00151	33500	0.122	0.0606	0.000515
SOL-njv_tee1	0.512	0.0527	1.89	0.00309	0.00186	<LOD	57.1	13.7	0.00397	0.00265	0.000691	1020	0.0403	0.0445	0.000293
SOL-bcr_bl1	2.51	0.0737	9.23	0.0063	0.00292	0.00177	113	0.95	0.00825	0.00614	0.00107	32500	0.0888	0.0366	0.000437
SOL-njv1_bl1	0.624	0.0383	2.23	0.00265	0.00133	<LOD	49.9	2.63	0.00352	0.00435	0.000465	965	0.0339	0.0193	0.000167
SOL-njv2_bl1	0.487	0.0397	1.79	0.00228	0.00122	<LOD	59.5	2.54	0.00319	0.00162	0.00046	1000	0.035	0.0246	0.00021
SOL-gbw1_mt2	0.551	0.554	21.8	0.0561	0.0332	0.0105	162	4.56	0.06	0.0981	0.011	7250	0.588	0.521	0.00474
SOL-gbw3_mt2	0.339	0.527	21.9	0.0595	0.036	0.0131	176	4.09	0.0636	0.0469	0.0117	7330	0.57	0.53	0.00534
SOL-njv_mt2	0.228	0.0435	1.94	0.00231	0.00111	<LOD	22.7	3.22	0.00268	0.00197	0.000448	271	0.035	0.0302	0.000149
SOL-gbw_tee2	1.52	0.632	23.9	0.0688	0.0394	0.0156	318	1.18	0.0761	0.196	0.0143	14400	0.603	0.655	0.00619
SOL-gbw_tee3	1.32	0.581	25.7	0.0642	0.037	0.0192	339	1.37	0.0699	0.243	0.0132	15400	0.646	0.607	0.00579
SOL-gbw1_tee4	2.32	0.61	25.4	0.0715	0.0384	0.0225	331	0.944	0.0755	0.168	0.0142	15100	0.687	0.635	0.00619
SOL-gbw2_tee4	1.42	0.589	25.6	0.0642	0.0356	0.0203	332	1.1	0.0666	0.149	0.0129	15400	0.636	0.637	0.00557
SOL-gbw_mt3	0.932	0.556	25.3	0.0626	0.0383	0.0147	320	0.825	0.07	0.233	0.0136	15600	0.514	0.579	0.00574
SOL-gbw_mt4	1.19	0.542	25.9	0.0569	0.0347	0.0105	324	0.19	0.0621	0.25	0.0117	16500	0.519	0.541	0.00559
SOL-gbw1_tee5	0.9	0.817	25.4	0.0857	0.0496	0.0162	324	0.946	0.0948	0.151	0.0172	15000	0.543	0.529	0.00774
SOL-gbw2_tee5	0.832	0.598	25.2	0.0608	0.0361	0.0104	312	0.665	0.0668	0.0841	0.0123	15900	0.516	0.524	0.00565
SOL-ncs_tee5	2.1	0.265	5.79	0.153	0.0818	0.0345	991	1.6	0.175	0.044	0.0293	9790	1.07	2.55	0.011
SOL-gbw_tee6	0.778	0.464	25	0.0507	0.0298	0.00827	301	0.195	0.0545	0.196	0.0103	16100	0.587	0.54	0.00468
SOL-ncs_tee6	2.11	0.287	6.07	0.16	0.0857	0.0371	1030	0.457	0.186	0.115	0.0309	10200	1.13	2.68	0.0118
SOL-gbw_tee7	1.07	0.516	25.2	0.0592	0.0358	0.0186	319	0.64	0.0655	0.207	0.0128	15600	0.515	0.556	0.00516
SOL-ncs_tee7	1.99	0.251	6.16	0.137	0.0746	0.0375	1180	1.52	0.155	0.0929	0.0282	10300	1.01	2.71	0.00952
SOL-gbw_mt5	0.811	0.496	23.1	0.0577	0.0348	0.0186	320	0.631	0.0622	0.229	0.0124	15800	0.514	0.569	0.00496
SOL-tw_bd1	48.9	7.6	41.4	5.25	2.64	1.11	45000	30.1	5.82	6.45	1.05	30500	49.4	40.2	0.417
SOL-tw_bd2	51.2	7.99	38.5	6.07	3.25	1.28	47800	26.7	6.55	4.76	1.22	26800	49.8	59.7	0.488
SOL-tw_bd3	107	7.59	34.8	5.3	2.92	1.15	45400	23.6	5.96	4.04	1.05	30700	45.2	49.8	0.443
SOL-tw_bd4	40.9	7.6	36.5	5.56	3.07	1.18	45300	98.6	6.18	4.35	1.1	30800	46	50.2	0.46
SOL-tw_bd5	107	7	35.2	5.13	2.69	1.14	43900	22.6	6.12	3.91	1.01	29000	42.9	47.9	0.435

Table B.13.: Reference samples, continued from table B.11

ProjNr	Mg	Mn	Mo	Na	Nb	Nd	Ni	P	Pb	Pr	Rb	S	Sb	Sc	Se	Sm
SOL-njv1_mt1	268	171	0.0132	26.5	0.00682	0.0231	0.317	197	0.435	0.00659	4.8	145	0.0178	0.00425	<LOD	0.00424
SOL-njv2_mt1	272	173	0.0124	28.8	0.00543	0.0211	0.297	201	0.476	0.00557	5.14	147	0.0159	0.00471	<LOD	0.00376
SOL-bcr_tee1	1480	81.4	0.866	3570	0.0307	0.087	4.54	2310	1.39	0.0223	34.8	2960	0.141	0.0179	<LOD	0.0148
SOL-njv_tee1	290	183	0.0174	40.1	0.0093	0.0199	0.405	214	0.601	0.00554	5.86	180	0.016	0.014	<LOD	0.0039
SOL-bcr.bl1	1450	80.5	1.05	2470	0.0247	0.0654	4.28	2270	1.27	0.0164	39.7	2860	0.0744	0.0113	<LOD	0.0125
SOL-njv1.bl1	274	172	0.0161	38.1	0.00508	0.0163	0.12	201	0.548	0.00452	4.64	145	0.0163	<LOD	14.8	0.00309
SOL-njv2.bl1	287	181	0.0119	31.4	0.00702	0.0173	0.13	214	0.514	0.0046	4.85	154	0.013	<LOD	4.78	0.00307
SOL-gbw1_mt2	1450	953	0.0714	99.4	0.0694	0.328	5.26	1330	1.41	0.0853	79.5	2070	0.0598	0.0355	0.0898	0.0625
SOL-gbw3_mt2	1440	342	0.0118	92.7	0.0163	0.331	4.91	1380	1.23	0.0873	85.2	2160	0.0378	0.0319	0.0374	0.0629
SOL-njv_mt2	215	138	0.0146	41.1	0.00732	0.0171	0.336	84.5	0.524	0.00472	5.28	74.7	0.0166	<LOD	<LOD	0.00301
SOL-gbw_tee2	2000	1200	0.0886	<LOD	0.102	0.372	5.11	2540	1.66	0.104	96.8	4070	0.0661	0.0773	0.462	0.071
SOL-gbw_tee3	2050	1200	0.0913	104	0.105	0.367	5.72	2570	1.53	0.101	89.1	4150	<LOD	0.0818	0.49	0.0707
SOL-gbw1_tee4	2040	1210	0.107	107	0.0765	0.399	6.06	2540	1.72	0.108	89.5	4120	0.0478	0.0823	0.339	0.0795
SOL-gbw2_tee4	2050	1220	0.0855	102	0.0893	0.361	5.59	2550	1.65	0.0986	88.5	4120	0.0584	0.0797	0.416	0.0702
SOL-gbw_mt3	2110	1280	0.0842	119	0.11	0.345	5.51	2740	1.61	0.095	118	4220	0.0652	0.0865	0.293	0.0701
SOL-gbw_mt4	2110	1520	0.0875	108	0.111	0.321	5.58	2750	1.52	0.0897	100	4500	0.0479	0.0812	0.0553	0.064
SOL-gbw1_tee5	2040	1060	0.132	110	0.12	0.514	6.18	2690	1.86	0.144	140	4430	0.0742	0.0814	0.0783	0.102
SOL-gbw2_tee5	2070	1050	0.0948	109	0.0793	0.35	6.02	2720	1.38	0.0985	105	4450	0.0579	0.0822	0.0581	0.069
SOL-ncs_tee5	4430	56.3	0.4	17900	0.409	0.985	1.4	897	42.5	0.269	4.73	7150	0.103	0.283	0.087	0.195
SOL-gbw_tee6	2040	1210	0.0786	110	0.094	0.296	6.53	2650	1.09	0.0844	80.7	4290	0.0483	0.0807	0.041	0.0647
SOL-ncs_tee6	4590	58.9	0.413	18500	0.454	1.06	1.37	927	44.8	0.29	5.1	7440	0.111	0.301	0.0869	0.213
SOL-gbw_tee7	2030	1250	0.103	108	0.116	0.352	6.19	2670	1.44	0.0995	95.4	4390	0.0533	0.0786	0.0553	0.0728
SOL-ncs_tee7	4840	60.8	0.407	18500	0.483	0.925	1.5	922	38.3	0.238	4.57	7760	0.101	0.293	0.0883	0.176
SOL-gbw_mt5	2080	1280	0.104	108	0.131	0.345	5.78	2710	1.55	0.095	95.2	4500	0.0537	0.0829	0.0552	0.0651
SOL-tw_bd1	22900	523	0.382	6360	19.2	35.5	70.9	383	44.1	9.59	178	4250	1.35	14.5	<LOD	6.45
SOL-tw_bd2	23200	555	0.384	6170	17.8	40.4	72.3	384	36.9	11.1	165	4340	1.11	14.8	<LOD	7.7
SOL-tw_bd3	22600	538	0.392	6630	17.3	36	71.7	398	34.1	10	152	4330	1.08	16.9	2.42	6.48
SOL-tw_bd4	22700	532	0.339	6740	16.7	36.7	72.6	396	36.6	10.2	154	4320	1.13	15.3	2.9	6.67
SOL-tw_bd5	23000	536	0.444	6640	17.4	36.7	67.6	366	37.8	9.85	142	4690	0.923	14	2.21	6.81

Table B.14.: Reference samples, continued from table B.11

ProjNr	Sn	Sr	Ta	Tb	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
SOL-njv1_mt1	0.0174	10.3	0.000356	0.00048	0.00592	2.24	0.134	0.00025	0.00354	0.164	0.127	0.0113	0.00407	34.9	0.164
SOL-njv2_mt1	0.011	10.5	0.000304	0.000421	0.00825	1.53	0.138	0.000211	0.00407	0.135	0.151	0.0148	0.00316	34.9	0.186
SOL-bcr_tee1	0.0547	21.5	0.00634	0.00159	0.0435	6.1	0.00609	0.000574	0.0179	<LOD	0.0583	0.0431	0.0079	28.6	0.258
SOL-njv_tee1	0.0276	11.3	0.00173	0.000512	0.00698	2.63	0.168	0.000239	0.00467	<LOD	0.355	0.0196	0.00515	38	0.112
SOL-bcr_bl1	0.0591	21.3	0.00475	0.00111	0.0305	5.31	0.00538	0.000442	0.0111	1.07	0.042	0.0365	0.00683	27.5	0.283
SOL-njv1_bl1	0.00921	10.6	0.000874	0.000382	0.00725	1.73	0.152	0.000199	0.00465	0.37	0.372	0.0159	0.00341	34.8	0.161
SOL-njv2_bl1	0.013	10.9	0.00107	0.000397	0.00683	2.35	0.154	0.000186	0.00438	0.35	0.0285	0.015	0.00421	36.8	0.0587
SOL-gbw1_mt2	0.19	31.3	0.00414	0.00923	0.149	28	0.0458	0.00502	0.105	0.746	0.0208	0.614	0.068	31.1	4.37
SOL-gbw3_mt2	0.0254	31.6	0.000447	0.0101	0.111	33.8	0.0423	0.00537	0.0899	0.73	<LOD	0.582	0.0738	34.7	2.13
SOL-njv_mt2	0.00713	10.9	0.000194	0.000342	0.00652	2.33	0.161	0.000179	0.00398	<LOD	0.147	0.0171	0.00261	36.1	0.0822
SOL-gbw_tee2	0.248	30.4	0.00794	0.0112	0.0906	28	0.0531	0.00606	0.0591	4.55	0.0832	0.684	0.0405	31.9	9.68
SOL-gbw_tee3	0.267	35.2	0.00802	0.011	0.113	29.4	0.0497	0.00569	0.0593	3.38	0.0427	0.647	0.0398	32.2	10.3
SOL-gbw1_tee4	0.14	33.8	0.00653	0.0125	0.0868	27.5	0.0512	0.00661	0.0574	3.03	0.0491	0.722	0.0408	32.9	7.28
SOL-gbw2_tee4	0.133	34.4	0.00561	0.0113	0.0781	26.6	0.0506	0.00572	0.0537	3.53	0.0299	0.681	0.038	32.8	6.96
SOL-gbw_mt3	0.237	31.4	0.00851	0.0106	0.0833	32.1	0.046	0.0061	0.0526	3.19	0.0493	0.642	0.0406	35.4	9.93
SOL-gbw_mt4	0.208	33.7	0.00777	0.00912	0.0743	32.1	0.0435	0.00536	0.0497	0.599	0.0422	0.643	0.037	34.6	11.6
SOL-gbw1_tee5	0.251	33.2	0.00443	0.0138	0.115	31	0.0602	0.00754	0.0691	0.649	0.12	0.971	0.0526	33.7	8.65
SOL-gbw2_tee5	0.198	31.9	0.00366	0.00979	0.0765	28.9	0.0459	0.0056	0.051	0.644	0.0462	0.689	0.0384	34.4	5.21
SOL-ncs_tee5	0.372	245	0.00998	0.0251	0.366	114	0.0202	0.0114	0.132	2.26	0.0657	0.989	0.0758	51.4	2.25
SOL-gbw_tee6	0.255	33.8	0.00717	0.00804	0.0725	29.6	0.0362	0.00455	0.041	0.65	0.041	0.54	0.0313	33.5	9.31
SOL-ncs_tee6	0.259	269	0.0285	0.0266	0.4	120	0.0214	0.012	0.136	2.4	0.0768	0.983	0.0805	53	4.75
SOL-gbw_tee7	0.393	36.2	0.00786	0.0107	0.0948	26.3	0.0468	0.00517	0.056	0.641	0.0974	0.626	0.0359	33.5	11.4
SOL-ncs_tee7	0.51	267	0.0318	0.0255	0.429	125	0.0212	0.00992	0.133	2.48	0.15	0.801	0.067	54	3.84
SOL-gbw_mt5	0.247	35.2	0.00907	0.0104	0.0922	34.7	0.0466	0.00503	0.0556	0.664	0.057	0.615	0.0347	34.6	11.4
SOL-tw_bd1	4.42	85.5	2.89	0.812	33.2	4190	0.84	0.422	8.1	109	277	37.7	6.15	113	153
SOL-tw_bd2	3.97	89.3	1.17	0.977	14.8	4280	0.839	0.494	3.63	111	1.71	32.4	3.44	126	169
SOL-tw_bd3	3.69	92.8	1.13	0.878	14	4230	0.794	0.429	3.5	108	1.45	29.3	3.06	117	134
SOL-tw_bd4	3.71	94.2	1.01	0.913	14.2	4260	<LOD	0.463	3.62	109	1.47	30.7	3.11	116	146
SOL-tw_bd5	3.69	89.8	1.07	0.842	12.7	4220	0.71	0.396	3.31	106	1.25	27.5	2.98	118	129

Table B.15.: Accuracy (in %) of references samples of the selected element analysis of ICP-MS and ICP-OES. Please note: This table contains all measured elements, including the elements of poor analytical quality.

Type	Species	ProjNr	Date.digestion	Al	As	B	Ba	Bi	Ca	Cd	Ce	Co
Plant	NJV 94-5 (wood fuel)	SOL-njv1_mt1	2011-07-01	-15.8	-36.8				-12.5	-11.8		
Plant	NJV 94-5 (wood fuel)	SOL-njv2_mt1	2011-07-01	-3.0	-10.7				-12.4	-17.6		
Plant	BCR- 129 (hay powder)	SOL-bcr_tee1	2011-08-30	5.2					-1.4			-41.8
Plant	NJV 94-5 (wood fuel)	SOL-njv_tee1	2011-08-30	-1.5	0.9				-6.5	-10.8		
Plant	GBW 10052 (Tea)	SOL-gbw1_mt2	2012-01-10		-11.7	630.5	-5.0	-23.0	-51.4	-0.4	0.1	-6.7
Plant	GBW 10052 (Tea)	SOL-gbw3_mt2	2012-01-10		-5.2	444.1	-8.2	-91.5	-50.2	-4.1	-3.6	-9.2
Plant	NJV 94-5 (wood fuel)	SOL-njv_mt2	2012-01-10	-7.2	7.8				-56.4	-11.7		
Plant	GBW 10052 (Tea)	SOL-gbw_tee2	2014-07-24		6.5	19.2	-5.5	-3.6	-7.5	1.1	17.3	-11.1
Plant	GBW 10052 (Tea)	SOL-gbw_tee3	2014-12-01		14.2	8.2	1.9	-14.4	4.2	-21.0	10.5	-12.6
Plant	GBW 10052 (Tea)	SOL-gbw1_tee4	2015-07-09		118.4	13.2	-5.1	-6.0	-6.9	-17.8	18.7	-16.4
Plant	GBW 10052 (Tea)	SOL-gbw2_tee4	2015-07-09		108.8	9.2	-3.6	-10.1	-5.5	-13.3	7.5	-6.3
Plant	GBW 10052 (Tea)	SOL-gbw_mt3	2016-05-15		-0.2	-82.4	-1.5	-21.5	-0.0	-0.4	3.5	-7.0
Plant	GBW 10052 (Tea)	SOL-gbw_mt4	2016-08-05		1.4	-67.2	-2.0	-33.1	-2.6	-5.0	-0.6	-6.9
Plant	GBW 10052 (Tea)	SOL-gbw1_tee5	2016-10-05		14.6	-47.8	-3.1	-2.6	-4.2	33.4	61.0	-18.2
Plant	GBW 10052 (Tea)	SOL-gbw2_tee5	2016-10-05		15.1	-43.1	-0.5	-24.5	-3.5	2.5	8.7	-9.0
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee5	2016-10-05	-0.6	-5.2	-77.2	-6.4	-44.6	-6.1	89.0	5.0	-10.4
Plant	GBW 10052 (Tea)	SOL-gbw_tee6	2017-03-07		4.1	-66.6	-4.9	-39.3	-3.1	-20.0	-4.4	-22.1
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee6	2017-03-07	5.5	-6.4	-81.8	-7.2	-40.7	-0.2	87.8	13.9	-10.5
Plant	GBW 10052 (Tea)	SOL-gbw_tee7	2017-04-07		15.6	-39.2	-6.3	-23.7	-4.1	2.3	4.2	-24.1
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee7	2017-04-07	7.3	10.0	-82.9	-2.7	-45.5	4.6	78.2	-8.0	-5.7
Plant	GBW 10052 (Tea)	SOL-gbw_mt5	2017-04-14		18.2	-53.8	0.1	-28.0	-2.0	4.1	0.2	-22.4
Rock	Clayey Shale 59	SOL-tw_bd1	2011-08-01	-3.2	-22.3		-1.4	29.9	-0.0	-13.6	-3.4	25.0
Rock	Clayey Shale 45	SOL-tw_bd2	2014-08-03	0.5	-17.0		-0.6	4.8	2.6	-11.5	14.8	-3.1
Rock	Clayey Shale 45	SOL-tw_bd3	2014-11-01	0.6	-9.5		-2.4	-7.4	4.3	-31.8	2.1	0.5
Rock	Clayey Shale 45	SOL-tw_bd4	2015-02-01	0.9	-9.3		-2.4	-9.6	4.3	-28.3	4.2	2.2
Rock	Clayey Shale 45	AMA-tw_ama1	2016-01-27	0.1	-0.9		-5.9	-33.5	3.1	-42.0	8.5	-5.4
Rock	Clayey Shale 45	SOL-tw_bd5	2016-01-27	-0.4	24.9		-5.1	-7.3	4.4	-22.6	4.7	-5.3
Rock	JLk- 1 (lake sediment)	AMA-jlk1_ama1	2016-01-27	1.8	9.6	-190.7	-0.6	-62.2	3.3	-35.0	10.8	0.7

Table B.16.: Accuracy, continued from table B.15

ProjNr	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Hf	Ho	K	La	Li	Lu	Mg
SOL-njv1_mt1	-47.7		-25.5				-29.7					4.7				-10.7
SOL-njv2_mt1	-30.8		-10.9				-28.2					8.3				-9.3
SOL-bcr_tee1	-7.8		-6.1				-0.9					-0.9				1.8
SOL-njv_tee1	-36.0		-14.1				-18.5					12.9				-3.4
SOL-gbw1_mt2	-40.1	-4.5	-9.2	-13.7	-10.3	-52.3	-49.6		-21.0		-15.4	-53.2	9.0	0.1	-23.6	-34.2
SOL-gbw3_mt2	-63.2	-9.1	-8.8	-8.5	-2.6	-40.3	-45.4		-16.4		-9.7	-52.7	5.6	1.9	-13.9	-34.4
SOL-njv_mt2	-71.4		-12.0				-67.5					-69.9				-28.2
SOL-gbw_tee2	65.0	9.0	-0.3	5.8	6.6	-29.0	-1.2		0.1		10.1	-6.8	11.6	26.0	-0.2	-9.3
SOL-gbw_tee3	43.0	0.2	7.3	-1.2	0.1	-12.9	5.3		-8.0		1.6	-0.9	19.6	16.8	-6.6	-6.7
SOL-gbw1_tee4	151.7	5.2	5.8	10.0	3.8	2.2	2.9		-0.6		9.2	-2.6	27.1	22.0	-0.2	-7.2
SOL-gbw2_tee4	54.3	1.6	6.7	-1.3	-3.9	-7.7	3.2		-12.4		-0.7	-0.8	17.8	22.5	-10.2	-6.7
SOL-gbw_mt3	1.3	-4.1	5.5	-3.7	3.6	-33.0	-0.6		-7.9		4.9	0.5	-4.8	11.3	-7.4	-4.2
SOL-gbw_mt4	29.4	-6.6	7.7	-12.5	-6.3	-52.5	0.6		-18.3		-10.2	6.2	-3.9	4.0	-9.9	-4.0
SOL-gbw1_tee5	-2.2	40.8	6.0	31.8	34.2	-26.4	0.6		24.7		32.0	-3.1	0.5	1.7	24.8	-7.5
SOL-gbw2_tee5	-9.5	3.1	5.2	-6.4	-2.3	-52.6	-3.0		-12.1		-5.1	2.7	-4.4	0.7	-8.9	-6.0
SOL-ncs_tee5	-19.1	-1.9	-12.3	18.0		-11.4	-7.4		-8.0	-70.7	-11.3	6.4	-14.8	-1.8	-0.1	-7.8
SOL-gbw_tee6	-15.4	-20.0	4.0	-22.0	-19.4	-62.4	-6.4		-28.3		-20.7	3.9	8.7	3.9	-24.6	-7.3
SOL-ncs_tee6	-18.7	6.1	-8.1	23.3		-4.8	-3.5		-1.9	-23.1	-6.3	10.7	-9.7	3.1	7.2	-4.3
SOL-gbw_tee7	16.2	-11.1	4.9	-8.9	-3.2	-15.4	-1.0		-13.8		-1.8	0.8	-4.7	6.8	-16.9	-7.6
SOL-ncs_tee7	-23.4	-7.2	-6.6	5.5		-3.9	10.3		-18.5	-38.1	-14.6	12.3	-19.5	4.3	-13.5	0.8
SOL-gbw_mt5	-11.8	-14.5	-3.8	-11.2	-5.8	-15.3	-0.5		-18.2		-4.6	3.2	-4.7	9.3	-20.0	-5.3
SOL-tw_bd1	-53.4	-2.6	18.2	-4.5	-14.7	-7.9	0.1	43.2	-1.4	37.2	-4.6	0.6	23.5	-16.2	-5.1	-2.7
SOL-tw_bd2	-51.2	2.5	10.1	10.3	4.8	6.5	6.3	27.3	11.1	1.3	10.6	-11.5	24.5	24.4	10.8	-1.2
SOL-tw_bd3	2.3	-2.7	-0.6	-3.7	-5.7	-4.1	1.0	12.5	1.0	-14.0	-4.3	1.5	13.0	3.7	0.7	-3.9
SOL-tw_bd4	-61.0	-2.5	4.2	1.0	-1.0	-1.3	0.6	369.4	4.8	-7.5	0.1	1.6	15.1	4.6	4.5	-3.4
AMA-tw_ama1	-51.9	-24.9	4.4	-20.7	-23.6	-21.6	-0.8	11.9	-18.6	-27.7	-19.9	-2.8	14.1	2.1	-14.5	-7.0
SOL-tw_bd5	1.7	-10.3	0.6	-6.7	-13.3	-5.1	-2.5	7.7	3.8	-16.7	-8.2	-4.3	7.2	-0.2	-1.2	-2.0
AMA-jlk1_ama1	-25.8	-8.8	6.0	-10.9	-7.8	-15.7	-1.4	16.3	2.3	-27.9	12.5	-2.5	6.5	0.1	-14.3	1.3

Table B.17.: Accuracy, continued from table B.15

ProjNr	Mn	Mo	Na	Nb	Nd	Ni	P	Pb	Pr	Rb	S	Sb	Sc	Se	Sm	Sn
SOL-njv1_mt1	-18.6		-33.7				-6.3	-36.1			-19.7					
SOL-njv2_mt1	-17.5		-27.9				-4.3	-30.0			-18.4					
SOL-bcr_tee1	13.0	-13.4	2.3				-2.0			-30.3	-6.3		5.0	-100.0		
SOL-njv_tee1	-12.7		0.3				1.7	-11.7			-0.1					
SOL-gbw1_mt2	-18.6	-35.1	-0.6	38.9	-6.2	-2.6	-52.6	-12.2	-8.3	-10.7	-50.7	15.0	-49.2	-10.2	-5.3	12.0
SOL-gbw3_mt2	-70.8	-89.2	-7.3	-67.4	-5.3	-9.1	-50.7	-23.0	-6.1	-4.3	-48.6	-27.3	-54.5	-62.6	-4.6	-85.1
SOL-njv_mt2	-34.3		2.9				-59.8	-23.0			-58.5					
SOL-gbw_tee2	2.6	-19.5		103.0	6.3	-5.4	-9.2	3.5	11.5	8.8	-3.1	27.1	10.4	362.4	7.6	46.0
SOL-gbw_tee3	2.9	-17.0	3.6	109.5	4.7	6.0	-8.2	-4.5	9.1	0.1	-1.3		16.9	390.0	7.1	57.2
SOL-gbw1_tee4	3.3	-2.7	6.6	53.1	14.1	12.3	-9.2	7.6	16.2	0.5	-1.9	-8.1	17.6	238.5	20.4	-17.7
SOL-gbw2_tee4	4.1	-22.3	1.6	78.6	3.0	3.5	-8.9	2.8	6.1	-0.6	-1.8	12.3	13.9	316.1	6.4	-21.9
SOL-gbw_mt3	9.3	-23.4	18.7	120.1	-1.5	2.1	-2.2	0.4	2.2	32.6	0.4	25.4	23.6	192.9	6.2	39.6
SOL-gbw_mt4	29.6	-20.5	8.1	122.9	-8.4	3.3	-1.8	-5.1	-3.6	12.7	7.2	-7.8	16.0	-44.7	-3.0	22.5
SOL-gbw1_tee5	-9.3	20.5	9.7	139.4	46.9	14.5	-4.0	16.3	54.9	57.8	5.5	42.7	16.3	-21.7	54.2	47.4
SOL-gbw2_tee5	-10.0	-13.8	8.9	58.6	0.0	11.4	-3.0	-14.0	5.9	17.9	5.8	11.3	17.4	-41.9	4.5	16.6
SOL-ncs_tee5	-7.7	42.8	-8.7		-1.5	-17.9	-10.3	-9.6	12.2	5.1	-2.0	8.8	-11.6	-27.5	2.9	37.8
SOL-gbw_tee6	3.1	-28.6	10.0	87.9	-15.4	21.0	-5.4	-32.2	-9.3	-9.3	2.2	-7.1	15.2	-59.0	-2.0	49.8
SOL-ncs_tee6	-3.4	47.6	-5.7		5.7	-19.4	-7.3	-4.7	21.0	13.4	2.2	16.8	-6.0	-27.6	12.2	-4.0
SOL-gbw_tee7	6.8	-6.0	7.7	131.7	0.6	14.7	-4.7	-9.8	7.0	7.2	4.6	2.5	12.3	-44.7	10.4	131.1
SOL-ncs_tee7	-0.4	45.3	-5.5		-7.5	-11.6	-7.8	-18.5	-1.0	1.5	6.3	6.7	-8.5	-26.4	-7.4	88.8
SOL-gbw_mt5	9.1	-5.1	7.7	162.6	-1.5	7.0	-3.2	-3.2	2.2	7.0	7.1	3.3	18.4	-44.8	-1.4	45.0
SOL-tw_bd1	-4.9	-20.3	-3.7	19.8	-6.7	-1.6	-2.5	16.0	3.2	14.7	6.3	35.2	3.2	-171.0	-6.5	34.0
SOL-tw_bd2	0.9	-20.0	-6.6	11.4	6.4	0.4	-2.3	-2.8	19.8	6.4	8.4	11.4	5.5	-134.9	11.6	20.3
SOL-tw_bd3	-2.2	-18.4	0.5	8.1	-5.2	-0.4	1.2	-10.1	7.7	-1.6	8.1	7.6	20.9	246.1	-6.1	11.9
SOL-tw_bd4	-3.3	-29.4	2.1	4.2	-3.4	0.8	0.6	-3.6	9.7	-0.9	8.1	13.3	9.1	313.7	-3.3	12.4
AMA-tw_ama1	-3.5	-20.4	-0.2	15.3	-20.9	-4.9	-8.1	-0.8	-13.3	-24.6	15.1	-19.3	0.3	288.7	-19.3	-9.0
SOL-tw_bd5	-2.5	-7.4	0.7	8.7	-3.5	-6.2	-6.8	-0.6	5.9	-8.4	17.4	-7.7	-0.3	215.3	-1.2	11.9
AMA-jlk1_ama1	-2.3	-33.8	5.1	9.6	-14.9	7.2	2.5	5.9	-6.2	-25.7	14.2	-11.7	-4.7	123.5	-19.8	-16.8

Table B.18.: Accuracy, continued from table B.15

ProjNr	Sr	Ta	Tb	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
SOL-njv1_mt1					-6.6								-8.1	
SOL-njv2_mt1					-36.2								-8.1	
SOL-bcr_tee1	-2.5				60.6								-10.9	
SOL-njv_tee1					9.6								0.1	
SOL-gbw1_mt2	-12.9		-19.0	88.8	33.4	-19.6	-14.9	124.3	24.4		18.2	79.1	-11.1	
SOL-gbw3_mt2	-12.3		-11.6	40.6	61.1	-25.7	-8.9	91.3	21.7		12.0	94.2	-0.9	
SOL-njv_mt2					-3.0								-5.1	
SOL-gbw_tee2	-15.6		-1.9	14.7	33.3	-6.9	2.8	25.7	658.7		31.6	6.5	-8.8	
SOL-gbw_tee3	-2.2		-3.2	43.7	40.0	-12.9	-3.5	26.3	463.3		24.4	4.7	-8.0	
SOL-gbw1_tee4	-6.2		9.7	9.9	31.1	-10.1	12.1	22.2	404.3		38.8	7.3	-6.1	
SOL-gbw2_tee4	-4.4		-1.2	-1.1	26.9	-11.2	-3.1	14.2	487.7		31.0	0.0	-6.3	
SOL-gbw_mt3	-12.8		-7.0	5.4	52.6	-19.3	3.5	11.9	432.2		23.5	6.7	1.1	
SOL-gbw_mt4	-6.3		-20.0	-6.0	52.9	-23.6	-9.2	5.8	-0.1		23.6	-2.6	-1.1	
SOL-gbw1_tee5	-7.9		21.4	46.1	47.7	5.6	27.8	47.1	8.1		86.7	38.3	-3.8	
SOL-gbw2_tee5	-11.4		-14.1	-3.2	37.5	-19.5	-5.0	8.4	7.4		32.4	1.1	-1.6	
SOL-ncs_tee5	-0.3		0.3	1.6	20.3			9.7	-5.7	9.4	45.4	20.3	-6.5	
SOL-gbw_tee6	-6.2		-29.5	-8.2	40.9	-36.4	-23.0	-12.8	8.3		3.8	-17.7	-4.3	
SOL-ncs_tee6	9.2		6.3	11.1	26.6			13.7	-0.0	28.1	44.6	27.8	-3.6	
SOL-gbw_tee7	0.6		-5.8	20.0	25.4	-18.0	-12.4	19.1	6.9		20.4	-5.6	-4.3	
SOL-ncs_tee7	8.6		3.2	19.0	31.6			11.2	3.4	149.9	17.9	6.3	-1.8	
SOL-gbw_mt5	-2.1		-8.6	16.7	65.1	-18.3	-14.7	18.4	10.7		18.3	-8.8	-1.2	
SOL-tw_bd1	-5.0	44.4	-4.5	155.7	-2.5	9.1	-15.6	145.5	3.5	13763.8	21.5	111.9	-1.6	-14.7
SOL-tw_bd2	-0.8	-41.3	15.0	13.8	-0.4	8.9	-1.1	10.0	5.6	-14.7	4.4	18.6	9.6	-6.1
SOL-tw_bd3	3.1	-43.5	3.3	7.7	-1.6	3.1	-14.3	6.1	3.2	-27.4	-5.4	5.4	2.2	-25.3
SOL-tw_bd4	4.7	-49.7	7.4	9.3	-0.8		-7.5	9.6	3.3	-26.4	-1.0	7.1	1.2	-19.0
AMA-tw_ama1	-0.8	-55.8	-13.2	-18.5	-2.0	-25.5	-25.3	-17.9	0.2	-26.4	-22.1	-12.0	-0.9	-27.1
SOL-tw_bd5	-0.3	-46.4	-0.9	-2.0	-1.9	-7.8	-20.8	0.2	0.7	-37.5	-11.4	2.6	2.8	-28.4
AMA-jlk1_ama1	-4.3	-35.6	-22.4	-19.0	1.3	-41.5	-8.7	-17.4	-0.7	392.8	-15.5	-16.6	-2.9	-25.2

Table B.19.: Precision (in %) of reference samples of the selected element analysis of ICP-MS and ICP-OES. Please note: This table contains all measured elements, including the elements of poor analytical quality.

Type	Species	ProjNr	Date.digestion	Al	As	B	Ba	Bi	Ca	Cd	Ce	Co
Plant	NJV 94-5 (wood fuel)	SOL-njv1_mt1	2011-07-01	7.4	32.6	105.2	1.2	13.5	0.2	3.4	28.2	1.9
Plant	NJV 94-5 (wood fuel)	SOL-njv2_mt1	2011-07-01	6.6	4.7	105.3	0.2	12.3	0.0	3.4	15.9	0.2
Plant	BCR- 129 (hay powder)	SOL-bcr_tee1	2011-08-30	8.4	72.0	95.7	0.2	31.8	0.9	1.0	43.3	23.5
Plant	NJV 94-5 (wood fuel)	SOL-njv_tee1	2011-08-30	8.2	7.8	6056.3	8.3	12.4	6.7	4.5	9.1	2.2
Plant	GBW 10052 (Tea)	SOL-gbw1_mt2	2012-01-10	5.5	10.4	1238.6	4.6	0.5	1.3	2.2	4.0	8.9
Plant	GBW 10052 (Tea)	SOL-gbw3_mt2	2012-01-10	1.1	3.8	897.0	7.9	89.1	1.3	3.7	7.5	11.4
Plant	NJV 94-5 (wood fuel)	SOL-njv_mt2	2012-01-10	3.5	7.5	105.2	2.3	0.7	3.2	8.3	10.6	8.3
Plant	GBW 10052 (Tea)	SOL-gbw_tee2	2014-07-24	1.7	8.2	118.5	4.2	24.5	2.2	1.7	12.6	3.2
Plant	GBW 10052 (Tea)	SOL-gbw_tee3	2014-12-01	4.5	16.0	98.2	1.9	10.5	6.8	15.7	6.0	1.4
Plant	GBW 10052 (Tea)	SOL-gbw1_tee4	2015-07-09	3.3	48.6	107.4	0.4	21.4	0.2	12.3	13.9	3.0
Plant	GBW 10052 (Tea)	SOL-gbw2_tee4	2015-07-09	1.8	42.1	100.0	2.2	16.1	1.7	7.4	3.1	8.6
Plant	GBW 10052 (Tea)	SOL-gbw_mt3	2016-05-15	1.1	1.4	67.8	3.2	1.4	4.7	0.2	0.7	7.9
Plant	GBW 10052 (Tea)	SOL-gbw_mt4	2016-08-05	3.4	9.0	39.9	1.7	13.6	2.1	4.6	4.6	8.0
Plant	GBW 10052 (Tea)	SOL-gbw1_tee5	2016-10-05	1.0	15.0	4.3	0.0	25.7	0.4	30.3	54.5	5.2
Plant	GBW 10052 (Tea)	SOL-gbw2_tee5	2016-10-05	0.3	15.4	4.3	2.6	2.5	1.1	0.1	4.3	5.5
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee5	2016-10-05	0.7	4.2	1153.8	0.3	6.0	2.4	3.7	2.7	4.8
Plant	GBW 10052 (Tea)	SOL-gbw_tee6	2017-03-07	0.5	4.3	38.8	0.6	21.7	1.5	19.7	8.3	9.6
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee6	2017-03-07	5.3	1.2	902.7	3.7	0.7	3.7	5.8	11.4	4.9
Plant	GBW 10052 (Tea)	SOL-gbw_tee7	2017-04-07	2.1	3.8	11.4	4.9	1.5	1.6	2.2	3.2	11.9
Plant	NCS DC 73349 (bush leaves)	SOL-ncs_tee7	2017-04-07	7.1	9.2	839.8	1.2	7.5	5.8	2.3	10.0	0.2
Plant	GBW 10052 (Tea)	SOL-gbw_mt5	2017-04-14	3.3	6.1	15.4	0.1	7.0	0.6	4.5	3.9	10.0
Rock	Clayey Shale 59	SOL-tw_bd1	2011-08-01	4.2	81.0	164.2	3.2	88.3	3.2	88.0	4.2	4.2
Rock	Clayey Shale 45	SOL-tw_bd2	2014-08-03	0.0	8.4	33.1	4.1	16.6	0.0	14.4	12.4	4.2
Rock	Clayey Shale 45	SOL-tw_bd3	2014-11-01	0.0	0.1	97.6	2.9	3.0	0.3	11.8	4.2	3.6
Rock	Clayey Shale 45	SOL-tw_bd4	2015-02-01	0.3	0.1	97.5	2.9	0.5	0.3	7.3	2.1	5.0
Rock	Clayey Shale 45	AMA-tw_ama1	2016-01-27	0.4	9.4	3.2	0.8	26.0	3.2	25.1	7.0	2.6
Rock	Clayey Shale 45	SOL-tw_bd5	2016-01-27	0.9	37.9	65.1	0.0	3.2	1.3	3.2	3.2	2.5
Rock	JLk- 1 (lake sediment)	AMA-jlk1_ama1	2016-01-27	0.9	1.9	6.9	3.2	21.2	1.9	24.6	9.4	3.2

Table B.20.: Precision, continued from table B.19

ProjNr	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Hf	Ho	K	La	Li	Lu	Mg
SOL-njv1_mt1	16.2	42.9	14.5	18.7	18.4	29.2	1.8	7.5	26.8	30.4	30.2	2.8	35.5	9.3	25.2	2.3
SOL-njv2_mt1	10.9	2.7	2.3	0.4	1.9	28.2	0.4	7.5	4.4	18.4	3.9	0.5	10.1	0.4	2.1	0.8
SOL-bcr_tee1	9.1	3.2	1.0	17.8	1.8	49.6	3.5	97.6	38.0	5.5	14.4	7.6	52.2	11.2	8.8	4.0
SOL-njv_tee1	2.5	24.5	4.7	17.2	37.1	100.0	13.9	106.5	7.7	18.4	42.9	4.8	6.9	79.7	42.8	5.7
SOL-gbw1_mt2	37.4	1.8	16.5	8.0	8.1	26.0	49.0	5.5	10.1	35.3	14.7	54.4	9.4	10.3	15.3	0.2
SOL-gbw3_mt2	61.5	6.6	16.2	2.5	0.3	7.5	44.8	5.5	4.8	35.3	9.1	53.9	6.1	8.7	4.5	0.2
SOL-njv_mt2	54.3	2.7	2.9	12.3	18.4	28.2	54.6	11.4	27.2	39.4	7.5	72.0	7.0	22.2	27.5	6.9
SOL-gbw_tee2	72.5	12.0	4.2	12.7	9.1	7.5	0.1	13.4	14.0	2.7	10.9	3.2	12.1	12.9	10.7	2.1
SOL-gbw_tee3	49.5	3.0	5.4	5.3	2.5	31.8	6.5	30.8	4.7	27.4	2.3	0.5	20.1	4.7	3.6	0.6
SOL-gbw1_tee4	163.1	8.1	4.0	17.2	6.3	54.6	4.0	9.6	13.1	12.1	10.0	2.3	27.7	9.3	10.7	0.1
SOL-gbw2_tee4	61.3	4.4	4.8	5.2	1.6	39.6	4.4	5.7	0.3	21.8	4.2	0.4	18.3	9.8	0.3	0.6
SOL-gbw_mt3	5.9	1.4	3.7	2.6	6.1	1.4	0.5	21.0	4.8	22.2	5.6	0.9	4.4	0.3	2.7	3.3
SOL-gbw_mt4	6.8	4.0	5.8	6.8	4.1	26.3	1.8	43.8	7.0	30.8	9.5	6.6	0.5	0.0	4.2	3.6
SOL-gbw1_tee5	8.1	44.7	4.1	40.4	37.4	14.1	1.7	47.8	41.9	24.6	33.0	2.8	5.2	2.2	38.5	0.2
SOL-gbw2_tee5	2.2	5.9	3.3	0.3	2.2	26.5	1.9	3.8	3.2	58.2	4.4	3.1	2.2	3.1	1.1	1.4
SOL-ncs_tee5	2.2	4.3	1.2	1.9	2.8	3.2	0.8	5.3	1.7	58.4	0.3	1.7	0.2	1.3	3.1	0.7
SOL-gbw_tee6	11.6	17.8	2.2	16.9	17.5	41.8	5.4	47.7	18.4	2.3	20.1	4.3	13.7	3.2	16.3	3.2
SOL-ncs_tee6	7.4	12.9	3.6	6.5	7.7	4.1	3.4	7.4	8.4	22.9	5.3	5.8	5.8	3.7	10.6	3.1
SOL-gbw_tee7	21.4	8.7	3.1	3.0	0.8	28.0	0.2	4.2	1.9	3.0	1.1	1.2	0.3	2.8	7.7	0.3
SOL-ncs_tee7	1.2	1.3	5.2	8.9	6.3	3.8	18.1	3.2	9.9	12.1	4.0	7.4	5.7	4.9	10.7	8.6
SOL-gbw_mt5	7.8	12.2	1.9	5.4	3.6	28.2	0.6	1.4	6.9	13.7	3.9	2.4	0.3	5.2	11.2	2.1
SOL-tw_bd1	3.2	86.4	3.2	92.5	91.6	92.7	2.2	4.2	92.7	90.3	92.8	2.2	4.2	3.2	72.5	3.2
SOL-tw_bd2	34.3	7.0	3.2	12.5	8.5	11.0	3.1	12.6	16.5	12.4	13.7	1.8	17.6	27.4	9.3	2.7
SOL-tw_bd3	37.2	1.6	0.8	1.8	2.4	0.0	0.9	0.5	5.8	4.6	1.5	0.7	8.7	6.2	0.7	0.0
SOL-tw_bd4	47.7	1.8	0.3	3.0	2.5	4.6	1.3	3.7	9.8	2.6	3.0	0.9	10.7	7.1	3.1	2.2
AMA-tw_ama1	35.8	21.6	0.6	19.2	20.8	18.3	2.6	1.0	17.9	19.9	17.6	3.6	9.7	3.7	15.6	1.2
SOL-tw_bd5	35.8	6.4	3.1	4.9	10.3	1.1	4.3	4.7	4.6	7.6	5.6	5.1	3.1	5.9	2.5	4.1
AMA-jlk1_ama1	4.2	20.2	2.6	18.0	16.8	16.0	1.8	3.5	15.7	23.1	17.2	2.5	8.1	4.0	14.1	0.2

Table B.21.: Precision, continued from table B.19

ProjNr	Mn	Mo	Na	Nb	Nd	Ni	P	Pb	Pr	Rb	S	Sb	Sc	Se	Sm	Sn	Sr
SOL-njv1_mt1	1.1	5.0	23.7	1.4	24.6	3.3	4.2	16.3	28.4	3.9	0.8	10.2	262.6	650.8	23.8	45.1	2.2
SOL-njv2_mt1	0.2	10.9	17.1	21.6	13.4	3.3	0.0	8.3	8.6	2.9	0.7	1.7	301.5	661.5	9.8	8.2	0.3
SOL-bcr_tee1	7.6	6.8	22.5	3.7	14.1	2.2	2.4	6.6	34.8	14.7	2.3	72.0	3.7	100.0	31.0	9.9	2.3
SOL-njv_tee1	6.0	25.3	14.7	34.4	7.0	32.0	6.3	15.7	8.0	17.3	6.8	1.0	1090.2	100.0	13.9	130.3	7.0
SOL-gbw1_mt2	13.8	14.7	7.2	26.1	6.0	8.6	49.9	1.4	12.7	12.1	33.1	3.3	56.5	68.4	10.8	6.5	10.3
SOL-gbw3_mt2	69.1	85.9	2.2	82.7	5.1	14.7	47.9	13.6	10.6	5.8	30.3	34.7	60.9	86.8	10.2	87.6	9.7
SOL-njv_mt2	2.2	5.0	18.3	5.8	7.9	31.1	57.9	0.9	8.0	5.8	55.7	2.8	268.6	100.0	12.2	40.6	0.5
SOL-gbw_tee2	0.8	5.8		8.0	5.7	15.1	4.0	16.2	6.1	7.0	1.9	14.2	5.3	62.9	0.2	21.9	3.2
SOL-gbw_tee3	0.5	9.0	3.8	11.5	4.1	4.9	3.0	7.2	3.9	1.4	0.2		0.2	72.6	0.9	28.3	0.8
SOL-gbw1_tee4	0.1	27.8	1.0	18.5	13.5	0.7	4.0	12.3	10.6	1.1	0.7	17.5	0.8	19.2	13.4	31.3	5.1
SOL-gbw2_tee4	0.7	2.1	5.6	5.0	2.4	7.1	3.7	7.3	0.9	2.2	0.7	0.9	2.3	46.5	0.3	34.8	7.1
SOL-gbw_mt3	5.7	0.6	10.2	17.2	2.1	4.2	3.3	12.7	2.7	30.5	1.6	12.6	6.0	3.2	2.2	16.5	2.3
SOL-gbw_mt4	3.6	4.5	0.4	18.6	8.9	3.7	3.8	1.0	8.2	10.9	8.4	17.2	0.7	4.2	8.6	3.2	5.0
SOL-gbw1_tee5	14.4	58.3	1.9	27.4	46.1	2.7	1.5	33.9	47.5	55.2	6.7	28.2	0.2	41.6	45.2	15.3	3.2
SOL-gbw2_tee5	14.9	13.3	1.1	15.6	0.6	0.0	2.6	1.0	0.8	16.1	7.1	3.2	0.7	5.1	1.5	8.8	0.7
SOL-ncs_tee5	11.0	35.9	7.3	4.3	0.3	5.0	2.6	1.3	0.6	16.9	0.6	2.4	2.6	3.9	2.9	15.8	2.9
SOL-gbw_tee6	0.3	6.1	2.1	3.2	15.9	6.3	4.2	21.9	13.6	10.8	3.4	16.5	1.2	25.8	9.1	116.8	5.1
SOL-ncs_tee6	2.2	40.4	4.3	15.8	7.0	3.5	0.7	4.0	8.5	26.1	4.6	10.0	3.7	3.8	11.9	15.9	6.3
SOL-gbw_tee7	3.3	23.5	0.0	23.3	2.2	0.7	0.8	3.8	1.8	5.5	5.7	7.9	3.7	0.0	4.0	92.9	3.6
SOL-ncs_tee7	3.1	38.3	4.1	23.1	6.4	5.9	0.1	11.0	11.2	12.9	9.1	0.4	0.8	5.4	7.4	2.1	9.2
SOL-gbw_mt5	5.5	24.7	0.0	39.7	2.4	0.2	2.3	1.0	2.8	5.3	8.4	7.2	1.6	0.2	7.1	18.4	0.8
SOL-tw_bd1	3.2	96.0	4.2	2.2	92.6	2.2	4.2	88.1	93.0	87.9	4.2	89.0	3.2	23.2	92.8	88.9	3.2
SOL-tw_bd2	4.0	9.5	0.0	3.1	14.1	3.2	1.9	3.4	10.4	9.1	5.0	4.9	4.5	109.1	13.4	7.4	3.1
SOL-tw_bd3	0.8	11.7	1.1	0.1	1.7	0.8	0.3	1.3	0.7	0.8	3.2	1.2	2.7	9.9	4.6	0.1	3.4
SOL-tw_bd4	0.4	3.4	2.8	3.5	3.7	0.4	0.3	8.7	1.2	1.6	0.0	6.6	8.7	7.7	1.8	0.4	5.0
AMA-tw_ama1	0.5	8.9	0.4	1.6	18.1	1.6	0.9	5.5	20.1	22.7	0.0	24.0	2.2	1.2	18.0	18.5	0.6
SOL-tw_bd5	0.4	26.7	1.3	4.1	4.2	0.3	0.4	5.7	2.4	6.1	1.9	13.1	0.6	17.9	0.3	0.2	2.2
AMA-jlk1_ama1	2.2	16.9	4.2	2.4	16.0	3.2	0.7	1.0	19.6	22.7	5.2	21.3	4.2	Inf	14.7	17.1	2.2

Table B.22.: Precision, continued from table B.19

ProjNr	Ta	Tb	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
SOL-njv1_mt1	42.1	17.4	14.2	12.9	12.7	22.3	16.3	9.8	14.2	26.8	8.8	0.0	20.0
SOL-njv2_mt1	50.6	2.9	19.4	22.9	9.6	2.8	3.6	9.8	1.3	4.0	15.6	0.0	36.0
SOL-bcr_tee1	87.7	18.8	102.1	0.7	13.4	3.8	117.6	100.0	38.6	5.2	7.3	6.3	4.7
SOL-njv_tee1	181.1	25.1	1.0	32.6	9.9	16.6	10.5	100.0	138.9	26.6	37.6	8.9	18.0
SOL-gbw1_mt2	38.6	11.4	76.4	18.7	1.7	11.8	91.0	76.3	51.8	4.3	4.1	7.8	47.3
SOL-gbw3_mt2	93.4	3.3	31.4	1.9	9.1	5.6	62.9	76.8	122.3	9.3	4.1	2.7	74.3
SOL-njv_mt2	68.4	16.3	5.6	4.9	5.4	12.6	5.8	162.8	1.3	10.7	30.3	5.4	39.7
SOL-gbw_tee2	17.8	7.3	7.2	0.5	13.9	6.5	7.0	44.6	79.9	6.5	1.7	4.7	16.9
SOL-gbw_tee3	18.9	6.0	34.2	4.6	6.6	2.2	7.5	7.3	7.7	0.7	3.2	3.9	24.9
SOL-gbw1_tee4	3.1	20.1	2.7	2.1	10.0	16.1	4.1	3.9	6.1	12.4	2.4	1.9	12.0
SOL-gbw2_tee4	16.7	8.1	7.6	5.3	8.6	0.4	2.7	12.0	35.3	6.1	4.5	2.1	15.9
SOL-gbw_mt3	26.2	1.8	1.5	14.0	1.2	7.2	4.7	1.4	6.7	2.2	1.9	5.6	19.9
SOL-gbw_mt4	15.3	12.5	12.2	14.1	6.6	5.9	9.9	4.2	8.8	0.1	7.0	3.4	40.7
SOL-gbw1_tee5	34.3	32.9	36.5	10.3	29.3	32.4	25.3	3.2	160.6	51.2	32.1	0.5	4.5
SOL-gbw2_tee5	45.7	6.0	9.5	2.7	1.4	1.6	7.6	0.7	2.2	7.2	3.5	2.8	37.1
SOL-ncs_tee5	62.5	3.4	5.4	8.1	1.5	3.2	5.8	3.9	13.0	17.4	1.8	2.7	35.5
SOL-gbw_tee6	6.3	22.8	14.2	5.2	22.2	20.2	25.7	0.2	11.4	16.0	21.4	4.2	12.5
SOL-ncs_tee6	7.0	2.4	3.5	13.7	4.5	5.2	2.3	1.9	1.8	16.7	8.1	0.3	36.0
SOL-gbw_tee7	16.6	3.1	12.1	6.3	0.4	9.2	1.4	1.1	110.8	2.5	9.8	0.0	37.6
SOL-ncs_tee7	19.4	1.7	10.8	18.2	3.5	12.9	4.5	5.4	98.6	4.9	10.1	2.2	9.9
SOL-gbw_mt5	34.6	4.2	9.0	23.3	4.2	11.6	0.8	2.4	23.4	4.2	12.9	3.2	37.2
SOL-tw_bd1	93.8	92.2	88.9	2.2	86.5	92.5	2.2	3.2	89.7	79.3	92.7	4.2	4.2
SOL-tw_bd2	4.0	11.6	12.7	1.6	13.7	8.8	8.9	2.2	14.1	5.5	12.2	1.7	22.9
SOL-tw_bd3	4.2	0.3	6.7	0.9	7.6	5.6	5.0	1.9	2.8	4.4	3.2	2.6	2.2
SOL-tw_bd4	11.0	4.2	8.2	1.1		1.9	8.5	4.2	1.4	4.2	1.7	3.5	6.0
AMA-tw_ama1	21.8	15.8	19.3	0.1	22.3	17.7	18.8	1.1	1.5	21.3	16.5	5.5	4.6
SOL-tw_bd5	5.2	3.8	2.9	0.1	3.7	12.9	0.9	0.6	16.3	10.4	2.6	3.2	6.3
AMA-jlk1_ama1	23.1	15.8	19.0	3.2	21.7	19.3	20.6	2.2	3.2	21.7	14.7	1.9	10.4

C. Mathematical Tools

Simple log-ratio:

$$\ln\left(\frac{x_i}{x_j}\right) = \ln(x_i) - \ln(x_j) \quad 5.1$$

(C.1)

additive log-ratio (Aitchison 1986):

$$alr(\mathbf{x}) := \left[\ln\left(\frac{x_1}{x_D}\right), \ln\left(\frac{x_2}{x_D}\right), \dots, \ln\left(\frac{x_{D-1}}{x_D}\right) \right] \quad 5.2$$

(C.2)

centered log-ratio (Aitchison 1986):

$$clr(\mathbf{x}) := \left[\ln\left(\frac{x_1}{g_m(\mathbf{x})}\right), \dots, \ln\left(\frac{x_D}{g_m(\mathbf{x})}\right) \right] \quad , \quad g_m(\mathbf{x}) := \sqrt[D]{x_1 \cdot x_2 \cdots x_D} \quad 5.3$$

(C.3)

Balanced log-ratio (Egozcue and Pawlowsky-Glahn 2005):

$$[r_1, \dots, r_N | s_1, \dots, s_M] := \sqrt{\frac{N \cdot M}{N + M}} \cdot \ln\left(\frac{\sqrt[N]{r_1 \cdot r_2 \cdots r_N}}{\sqrt[M]{s_1 \cdot s_2 \cdots s_M}}\right) \quad 5.4$$

(C.4)

Figure C.1.: Biplots of the PCA of vratios between shoot tips of *C. sinensis* and corresponding soil analysis. Labels of elements do not overlap for visibility.

D. Geochemical Characterization of Tea and Soil

Figure D.1.: Graph of ilr-ANOVA (CoDa dendrogram) for shoot tip samples and black processed teas. For calculating the ilr-ANOVA an element subcomposition was used which excludes elements with high probability to be altered by correction for AP (Section 6.4) and by leaf development stage (Section 7.4.1), but including Sn in the upper graph, and including Al in the lower graph.

Table D.1.: List of elements by parameter which affect log-ratios of element concentrations.

Parameter	Affected elements	Unaffected element sub-composition
Correction for adhering particles	Th, Ta, Hf, Zr, U, Nb, Ti	Al, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Sm, Sr, Tb, Tl, Tm, Y, Yb, Zn
Leaf development stage	Al, Sc, Ba, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sr, Tl, Zn
Tea manufacturing	Sb, Pb, Cr, Sc	Ca, Cd, Co, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Rb, S, Sr, Tl, Zn
Soil management	S, P, Ca, (K)	Cd, Co, Cs, Cu, Fe, (K), Li, Mg, Mn, Mo, Na, Ni, Sr, Tl, Zn
Intra-location variability	Al, Ba, Cd, Cr, Cu, Fe, Li, Mg, Mo, P, S, Sc, Sr, Zn	Ca, Co, Cs, K, La, Mn, Na, Ni, Pb, Sb, Tl, Y

Table D.2.: List of elements by nutrient status for *C. sinensis*.

	elements
macro-nutrients	K, Ca, P, Mg, S
micro-nutrients	Cu, Fe, Mn, Mo, Ni, Zn
beneficial elements	Al, Co, La, Y, Na, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
non-nutrients	Ba, Cd, Cr, Cs, Li, Pb, Rb, Sb, Sc, Sr, Tl

D. Geochemical Characterization of Tea and Soil

Figure D.2.: Vratios of subsoil/upper crust, grouped by tea growing regions. Elements are ordered by median of vratio.

E. Provenance Analysis

Table E.1.: List of elements for suitability for provenance analysis: Each element has for each influencing parameter a weight. If the parameter influences the element strongly the weight is set to zero. If the parameter has no influence on the element concentration the weight is high. For each the parameter the weight are multiplied with a factor, depending on the impact these factors are 1, 2, or 3. The sum of all weights per element is an indicator how robust the respective element is for provenance analysis, the higher the value, the better.

	intra-garden variability	sink/source pairwise log-ratio	sink/source pairwise log-ratio sum p-value	sink/source distribution	manufacturing	soil management	sink/subsoil pairwise log-ratio	sink/topsoil pairwise log-ratio	sum
Al	0	0	0	4	6	6	3	1	20
Ba	1	0	0	0	6	6	0	1	14
Ca	2	4	1	4	6	0	0	1	18
Cd	0	2	0	0	6	6	6	2	22
Co	2	4	1	0	6	6	6	2	27
Cr	1	4	1	0	0	6	6	2	20
Cs	2	4	1	4	6	6	6	1	30
Cu	0	4	1	4	3	6	6	2	26
Fe	0	0	0	0	6	6	6	1	19
K	2	4	1	4	6	3	0	2	22
La	2	4	0	0	6	6	6	1	25
Li	1	4	1	0	6	6	0	1	19
Mg	0	4	0	0	6	6	6	2	24
Mn	2	4	1	4	6	6	6	2	31
Mo	1	2	1	0	6	6	3	2	21
Na	2	2	0	0	6	6	0	0	16
Ni	2	4	1	0	6	6	0	0	19
P	0	4	1	4	6	0	0	2	17
Pb	2	4	1	0	0	6	6	2	21
Rb	1	4	1	4	6	6	6	2	30
S	0	2	0	4	6	0	0	2	14
Sb	2	4	1	4	0	6	6	2	25
Sc	0	0	0	0	6	6	0	0	12
Sr	0	4	1	4	6	6	6	2	29
Tl	2	4	1	0	6	6	3	1	23
Y	2	4	0	0	6	6	0	1	19
Zn	0	4	1	0	6	6	6	2	25

Figure E.1.: Histogram of the first score of weighted linear discriminant function for shoot tip and processed tea samples from Darjeeling and Assam. The subcomposition includes the elements Al, Mg and Tl, and excludes Rb. Samples are colored by Subgroup. Total number of samples is $N = 162$ (Darjeeling $N = 136$, Assam $N = 26$). Clr-scalings for LD1 and misclassifications are listed in Table E.2.

Table E.2.: Clr-scalings of weighted LDA (upper table) and misclassifications (lower table) for discrimination of tea from Assam and Darjeeling. The element compilation includes Al, Tl and Mg, and excludes Rb. Table corresponds to Figure E.1). The rows of the misclassification table give the number of samples predicted into respective group.

	Co	Cs	Mn	Sr	Zn	Mg	Al	Tl
1	-0.26	0.02	-0.10	0.84	0.86	-1.78	1.07	-0.65

	Assam	Darjeeling
Assam	14	12
Darjeeling	0	136

E. Provenance Analysis

Figure E.2.: Histogram of shoot tip and processed tea samples displaying the first score of linear discriminant function separating two metamorphic zones of Darjeeling. The element compilation includes Ca, K and Y, and excludes Co, Cs and Rb. Samples are colored by location in Darjeeling District. Only samples with high certainty of source rock are included (Table 9.6). Total number of samples is N = 71 (Grt+Mu Gneiss N = 29, St Gneiss N = 41). For abbreviations see caption of Table 9.6. Clr-scalings for LD1 and misclassifications are listed in Table E.3.

Table E.3.: Clr-scalings of LDA (upper table) and misclassifications (lower table) for discrimination of tea from to metamorphic zones in Darjeeling. The element compilation includes Ca, K and Y, and excludes Co and Cs. Table corresponds to Figure E.2). The rows of the misclassification table give the number of samples predicted into respective group.

	Mn	Sr	Zn	Ca	K	Y
LD1	-2.45	-2.89	0.85	5.82	-2.08	0.75
	Grt+Mu Gneiss			St Gneiss		
Grt+Mu Gneiss	28			1		
St Gneiss	3			38		

Curriculum Vitae

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School

1996 – 2004	St.Raphael-Gymnasium, Heidelberg, Germany
2000 – 2004	Participant of Heidelberger Life-Science Lab
Summer 2003	Participation in 1st International Summer Science Camp of XLab, Göttingen, Germany
Summer 2004	Participation in 36th ISSI (Dr. Bessie F. Lawrence International Summer Science Institute) of the Weizmann Institute, Israel
July 2004	Participation in the 55. Nobel Laureate Meeting in Lindau 18. Nobel Laureate Meeting of Physics

Study - Diploma

10/2004 – 09/2007	Study of Geosciences with specialization in Geophysics at Friedrich-Schiller-University Jena, Germany
10/2007 – 07/2008	Study at Universidad Complutense Madrid (UCM), Spain, Sección Departamental de Astronomía y Geodesia
08/2008 – 09/2008	Internship at UAF/AVO (University of Alaska Fairbanks/ Alaska Volcanic Observatory), Supervisor: Dr. Jessica Larsen
10/2008 – 05/2012	Study of Geosciences with specialization in Geochemistry at Georg-August-University Göttingen, Germany
08/2009 – 10/2010	Geological Mapping Project in SE-Sweden: <i>Geologische Kartierung metamorpher und granitoider Gesteine der Transskandinavischen Magmatischen Zone, NE' Vättervik (SE-Schweden)</i> , Grade 2,0
02/2011 – 04/2012	Diploma Thesis <i>Geochemical investigation on the tea plant Camellia sinensis: Implications from element soil-plant transfer factors for provenance studies – the case of Darjeeling Tea from NE-India</i> , Grade 1,0
14.05.2012	Diploma in Geosciences

Study - PhD

12/2012 – 07/2018	PhD Study at Georg-August-University Göttingen, Germany
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