GEO 511: MASTER THESIS

Soil analysis at Mount Etna to explain faster tree growth preceding a volcanic eruption

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Abstract

In the year 2003, Mount Etna (Sicily, Italy) erupted on its north-east flank. The assessment of remote sensing images revealed an enhanced normalized difference vegetation index (NDVI) signal, indicating higher plant activity on a distinct line in the years 2000 to 2003. The line lies on exactly the same spot where later the eruption occurred. Since then the trees have been investigated and larger tree rings in the year before the eruption could indeed be found, thus supporting the remote sensing data. However, it remains unclear why the enhanced activity of the plants occurred. In this thesis, soil was sampled at the eruption site at Mount Etna. Ten soils from trees which had evidentially grown faster and ten soils at control sites were sampled and analysed for the bulk dry density, pH, total carbon, hydrogen and nitrogen, ammonium, nitrate, phosphorus and potassium. These factors were statistically tested for differences. Only pH and total carbon differed significantly between the two groups. However, pH varied only around 0.1, which is very little in soils, whereas total carbon was lower in those soils, where the trees grew faster. An explanation might be, that the decomposition was also enhanced before the eruption. All other nutrients did not differ significantly, indicating that there indeed never was a big difference or it has disappeared again in the ten years after the eruption. To solve the question of the enhanced plant growth it is therefore necessary to investigate other properties as isotopes or gas emissions. Furthermore, it would be obviously helpful to find more lines with a NDVI signal on Mount Etna or other volcanoes, to be able to research this topic more profoundly.

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1. Introduction

1.1. Volcanoes

Volcanoes are one of the major drivers, forming and shaping our earth. Although they only make up a tiny part of the earth’s surface, the products of these volcanoes, namely volcanic rocks, make up over 80% of our planet’s crust (Press and Siever 2003).

Since the formation of the earth, volcanoes played a very important role in creating the atmosphere by outgassing of CO_2 and other volatile elements (Schmincke 2000). Furthermore, they still constantly reproduce oceanic lithosphere at the mid-ocean ridges (MOR) which is subducted at the plate borders under either another oceanic or a continental plate. Due to this reproduction, only little oceanic crust is older than 150 million years (Press and Siever 2003).

Fascination for these forces of nature has been great ever since human beings came across it, still it took a very long time until the understanding of volcanoes began to move in a convenient direction. It was not until the middle of the 20th century that the theory of plate tectonics, first delineated by Alfred Wegener 1911, was getting accepted. With this, it was possible to explain volcanoes as the exit of material (which is called magma inside the earth and lava as soon as it reaches the atmosphere) originating from the earth’s mantle (Giese 1987).

Today’s 550 active sub-aerial (not being under water) volcanoes vary a lot in their magmatic composition, as well as in their frequency and intensity of eruptions (Sinkin and Siebert 1984).

Generally, acidic magma, which is rather viscous, tends to produce more explosive eruptions (e.g. the Vesuvius) than basic magma, which is usually more fluid and just flowing out of the crater (e.g. in Hawaii).

The classical type which is commonly known and wide spread on earth is the so called stratovolcano (figure 1, e.g. Mount Etna). It represents a mixture of explosive emission and fluid effusion. The intermittent layering of these two depositions is very much characteristic for a stratovolcano (Rast 1983).

The unconsolidated material which is transported through the air from a volcano and falls out around it is called tephra (greek: ash, after Aristoteles) and can be divided into blocks

(>64mm), lapilli (lat.: stones; <64mm); coarse ash (<2mm) and fine ash (<0.063mm) (Fischer and H.-U. 1984; Schmincke 2000).

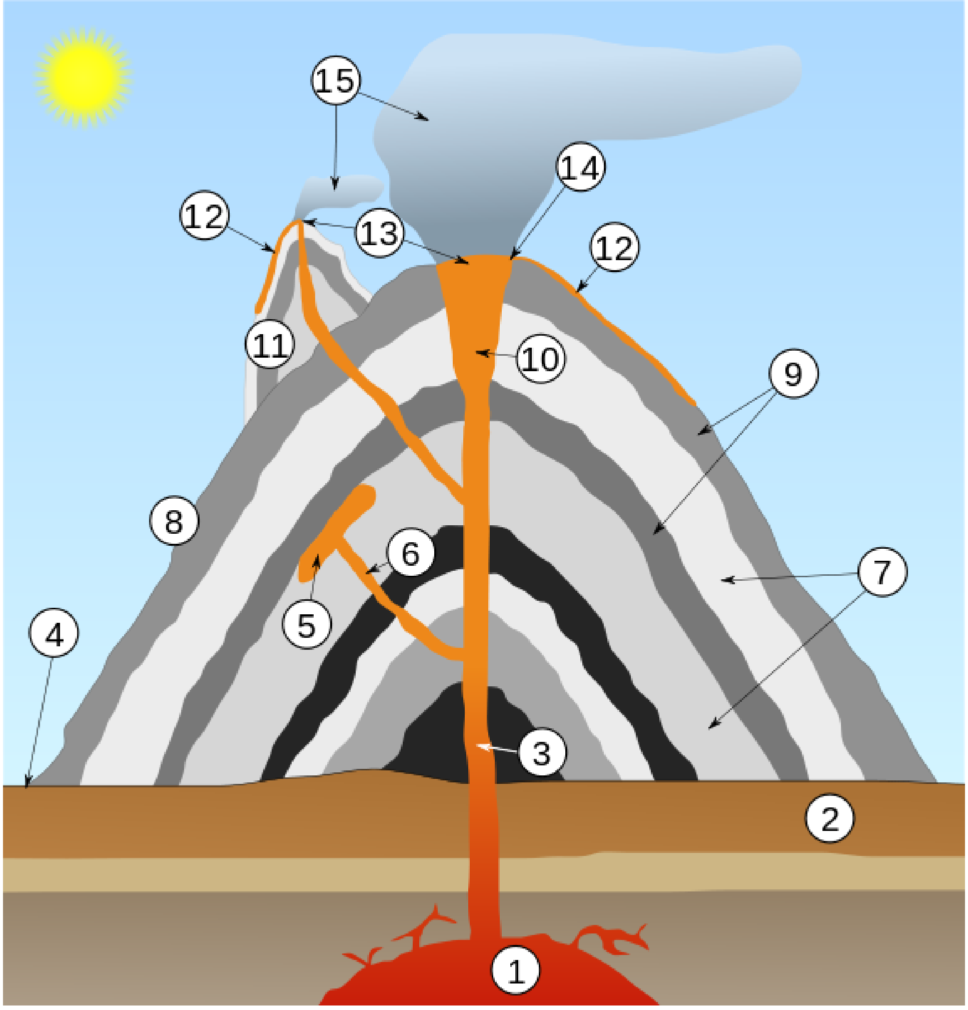


Figure 1: Schematic of a stratovolcano (vertically exaggerated).
1: magma chamber; 2: bedrock; 3: conduit (pipe); 4: base; 5: sill; 6: branch pipe; 7: layers of ash emitted by the volcano; 8: flank; 9: layers of lava emitted by the volcano; 10: throat; 11: parasitic cone; 12: lava flow; 13: vent; 14: crater; 15: ash cloud (Messer, 2006).

Although it is commonly known that volcanoes can pose an immediate threat to their environment (see chapter 1.2.) a lot of people have always been living in the surroundings of active volcanoes, because the soils around them are often very fertile (see chapter 1.3.).

1.2. Volcanic Hazards and Risk Management

Volcanoes have always been posing high dangers for the people living around them. Above all, irregularly erupting, very explosive volcanoes have made it to our history books. Since 1700 more than 260000 people have been killed by volcanic events (Tilling and Lipman 1993).

There are many infamous disasters related to volcanoes, like the eruption of Santorini around 3600 years before present, which destructed nearly all the island and extinguished the entire population living on it (Manning et al. 2006). The destruction of Pompeii 79 AD by the Vesuvius was the first written description of an eruption by Pliny the younger in his second letter to Tacitus.

More recent events were for example the devastating eruptions of Tambora (Indonesia) 1815/16, causing between 66000 and 92000 deaths, and Krakatao (Indonesia) 1883, causing more than 36000 deaths. Through the enormous amount of dust which was thrown high into the atmosphere by Tambora and Krakatao solar insolation was dimmed and a decrease of some degrees Celsius in the annual mean air temperature of the earth in the year after the eruptions had been recorded (Rast 1983).

One of the best researched eruptions is the one of Mount St. Helens (Washington, USA) 1980, as the USA had the interest, institutions and the money to investigate this eruption inside their own country (Schmincke 2000).

Even in the year 2010, the eruption of Eyjafjallajökull (Iceland) drew much attention on it, as it brought large parts of the air traffic of Europe to its knees. The cause for this was the ash cloud, which distributed over a huge area and posed a direct danger for the airplane engines.

There are several dangerous mechanisms possible at a volcanic eruption (after Schmincke, 2000):

- Tephra fallout.
- Pyroclastic flows: large and quick mass flows with up to 800°C hot erupted material. Probably the most deadly mechanism.
- Lahars: mud and debris flows, happening when water destabilizes freshly erupted pyroclastic material and/or tephra.
- Lava flows.
- Ash clouds, endangering mainly air traffic.
- Various other mechanisms like volcanic gases, tsunamis, earthquakes, etc.

Knowing about all these hazards, it seems obvious to use as much effort as possible to monitor and investigate active volcanos to reduce possible damage to people and goods.

Volcanoes are nowadays monitored for seismic activities, gravimetric, magnetic, thermal or surface deformation anomalies, outgassing and gas composition, using stationary devices as well as satellite based remote sensing approaches (Keller 2004). However, eruptions can occur without long precursor events, which are measurable with these mentioned methods.

Additionally to the extreme difficulties in forecasting volcanic eruptions, there is often an insufficient risk management. The civil protection plan for the region around the Vesuvius (Dipartimento della Protezione Civile 1995) for example was recently heavily criticised for being politically motivated and far from sufficient (Rolandi 2010). Not only the borders of the red emergency zone (the zone of the highest danger) follow administrative borders and not a distinct distance to the crater, but furthermore, they used the last large eruption from 1631 as reference for the whole emergency plan, although it might be possible that a future eruption could be far more powerful (Marzocchi et al. 2004). Thirdly, at this 1631 eruption, ground deformations could be monitored two weeks before, thus the whole emergency plan is based on the assumption that the authorities have two weeks of time to decide and act. This is indeed highly questionable, as we have yet no invariably working forecasting possibility of volcanic eruptions even on this timescale (Kilburn 2003; Solana et al. 2008).

The complexity of assessing volcanic hazards and implementing emergency plans emphasises the need for better and long term forecasting possibilities as well as a more profound understanding for the processes happening in and on a volcano before and during an eruption.

1.3. Volcanic Soils

Generally, all soils are the result of different pedogenic factors. These factors have been defined as climate, parent material, topography, time and organisms (Jenny 1941). The one factor, which distinguishes volcanic soils from all others is the parent material. This parent material are the volcanic rocks, or more precisely the lava and tephra which give volcanic soils unique properties, often making them very fertile. Firstly, ash particles are very porous, leading to a high water retention capacity and working as natural water repository. Secondly, young volcanic rocks are often very rich in trace elements and nutrients. Thirdly, tephra and also lava flows have often vitreous properties, which react with clay minerals more quickly than crystalline rocks (Schmincke 2000).

However, volcanic soils are retaining pollutants well, which is causing problems in agriculturally used regions. Furthermore, these soils, having high porosity and low density, are very susceptible to erosion, landslides or debris flows (Arnalds and Stahr 2004).

The classical young volcanic soil is classified as Andosol (WRB 2006). By definition, Andosols have either andic or vitric properties. The andic property is defined as having at least two percent of aluminium and iron, not more than 0.9 g cm^{-3} as bulk dry density, at least 85 percent phosphate retention capacity, and less than 25 percent of organic carbon. On the other hand, vitric means that the soil has at least five percent of volcanic glass in the fine earth fraction, at least 0.4 percent of aluminium and iron, at least 25 percent phosphate retention capacity and less than 25 percent of organic carbon.

Volcanic soils are not limited to Andosols. Often other soil types are formed, mostly with increasing age. Still, Andosols are the most characteristic volcanic soils and the important ones regarding this piece of work.

1.4. Scientific Background

Many effort has been put into the investigation and the research of volcanoes and their hazards. Still they are a matter of debate and eruption forecasting remains very difficult (Kilburn 2003; Solana et al. 2008). In recent time, monitoring mainly focussed on seismic activities and ground deformation patterns. However, the investigation of volcanic degassing products obtained more and more interest as well, for example on Mount Etna and the Vesuvius (Aiuppa et al. 2013; Caliro et al. 2005; Giammanco and Bonfati 2009). Concerning vegetation or soil properties and their behaviour before and during eruptions, there is even less research to be found. Although nearly forty years ago a paper was published describing changing vegetation patterns, preceding an eruption (De Carolis et al. 1976), no or little effort has been put since then to further investigate this.

By chance, a vegetation pattern was found on Mount Etna, preceding the 2003 eruption by Houlie et al. (2006). They used the NDVI, which accounts for the greenness of plants and thus their photosynthetic activity, to find a distinct line of around 3 km length at the NW slopes of Mt. Etna.

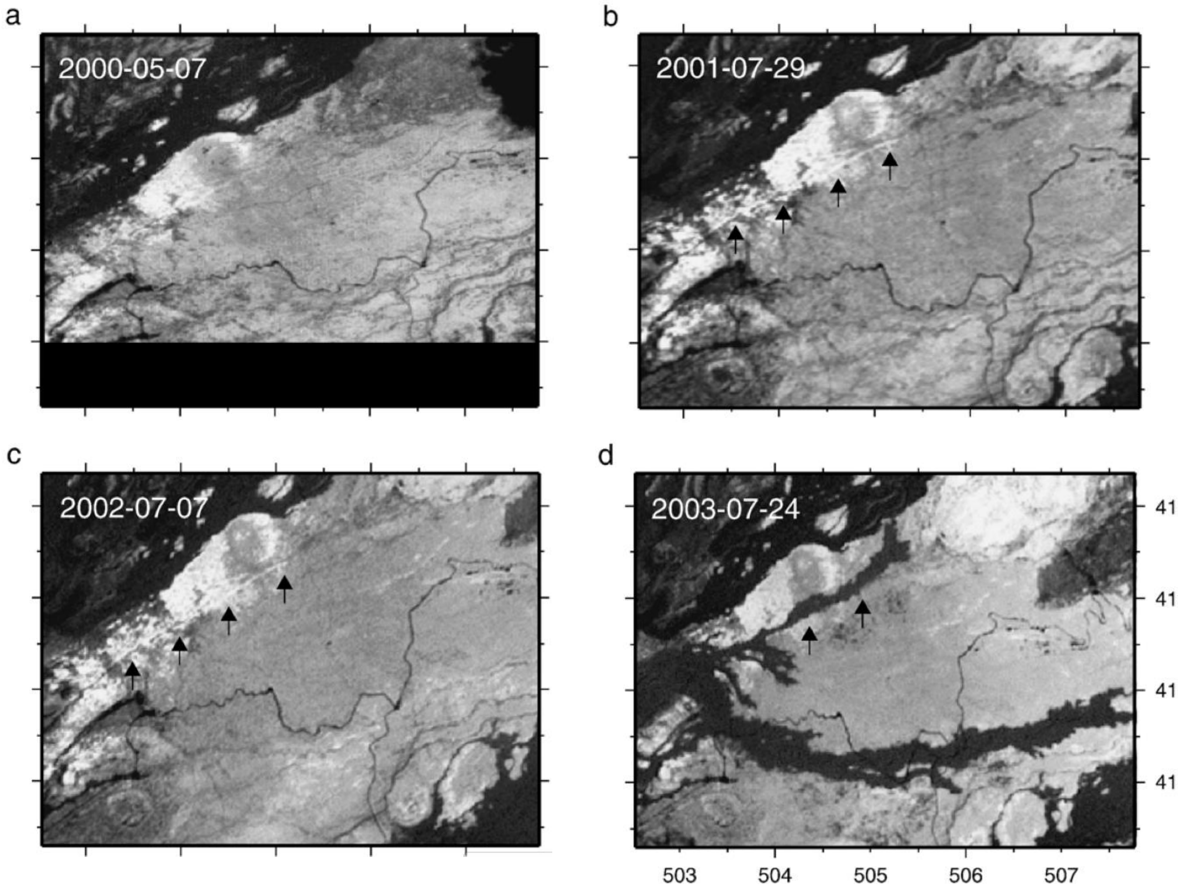


Figure 2: ASTER satellite images (resolution: 60m) of the north west flank of Mt. Etna.
***A**: 7. May 2000. A very faint bright line is forming. **B**: 29. July 2001. The line is bright and clearly visible. **C**: 7. July 2002. The line remains bright. **D**: 24. July 2003. Lava coveres the area, where the line was. (Houlie et al. 2006)*

Tree-ring measurements support the fact that some trees indeed grew faster during the time before the eruption took place, compared to other years and compared to trees not directly standing at the line (Seiler et al., in progress). There are different hypotheses trying to explain the enhanced NDVI signal, including CO_2 degassing, temperature gradients, warm fluids or ground deformation (Houlie et al. 2006). Yet no evidence has been found to clearly support one of these explanations. Strong degassing of CO_2 should result in lower ^{14}C values, as volcanic gas is completely depleted in ^{14}C. However, this could not be shown in an earlier master thesis, at least not for an older eruption on Mt. Etna with very similar patterns (Sonzogni 2011). More effort should therefore be put into finding alternative explanations.

1.5. Research Goal and Hypotheses

Knowing about the weaknesses of volcanic eruption forecasts and the need to improve the understanding of measurable processes happening prior to eruptions, I will focus in this thesis on the vegetation anomaly on Mount Etna in the years 2000-2003. As it seems proved that trees on the enhanced vegetation line indeed grew faster and the reason for this is still a matter of debate, the aim of this work is to find an explanation in the volcanic soils around the relevant trees.

The trees could have been affected by nutrients, transported by fluids or upwelling from deeper ground layers. This should not only leave a trace at the trees, but also in the soils beneath them. I therefore hypothesize, that:

1. The difference in growth on the enhanced NDVI line compared to outside this line is a cause of soil property changes.
2. The amount of nitrogen, phosphorus and potassium or a part of them are factors in the soil which induced the difference.
3. pH changed, due to gas or fluids in the ground and potentially influenced nutrient availability.

2. Material and Methods

2.1. Study Area

2.1.1. Geographic and Climatic Situation

Mount Etna lies in the north-east of Sicily, around 34°40’ N / 15°00’ E. With its peak at 3323 m a.s.l. it is not only the highest mountain of Sicily, but also the largest active volcano in Europe. It is surrounded by the large town of Catania in the south with more than 290000 inhabitants, and smaller villages like Randazzo in the north, Giarre in the east and Bronte to the west. Mount Etna is furthermore one of the most active volcanoes on earth, with its regularly up to years or decades lasting eruptions. Only five volcanoes on earth are as active as Etna. The start of the volcanic activity is assumed to be around 500000 before present (Branca et al. 2007). The focus of the volcanic activity lies on the summit and three radial rift zones (structures of extension, where magma can rise up): the NE rift, S rift and W rift (Acocella and Neri 2003).

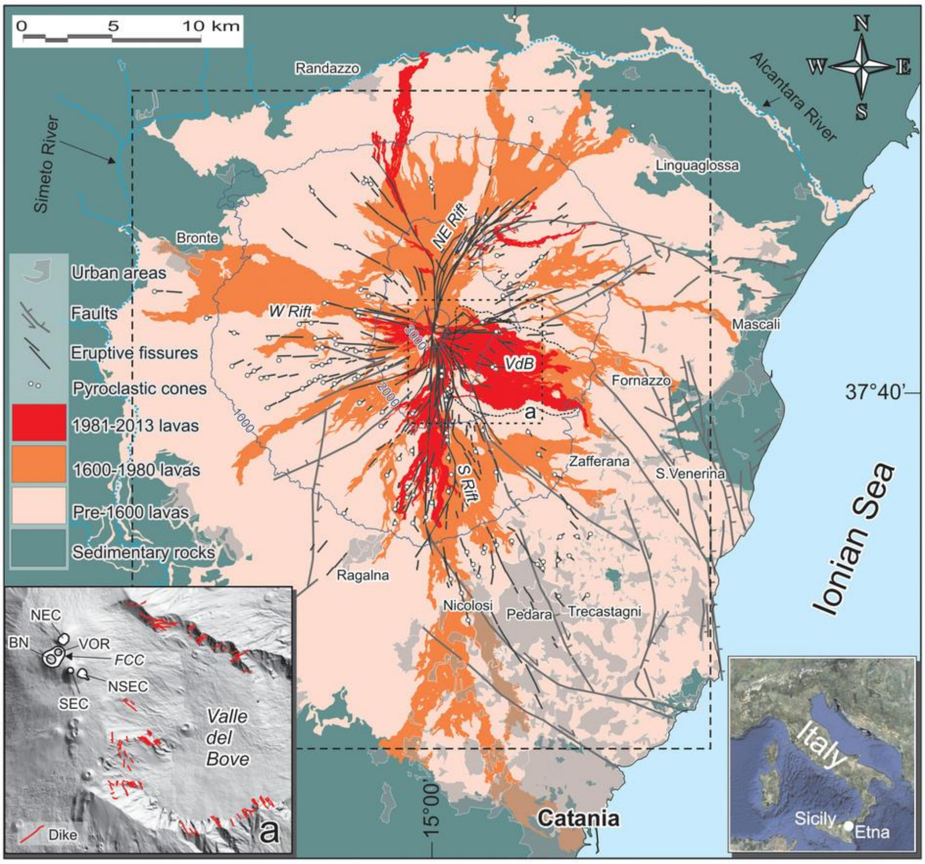


Figure 3: Volcanic map of Mount Etna (DelNegro et al. 2013).

Mt Etna is a classical stratovolcano with layers of lava, as well as of tephra. The steepness of the flanks increases with higher altitude from 2-5° at the bottom, up to 25° towards the summit. The fundament of Etna consists of Pleistocene (the last 2.5 million years, excluding the last 12’000 years) sediments, which rises around 1200 m a.s.l. The upper part of the volcano is completely built up of originally volcanic rocks (Pichler 1984; Tanguy et al. 1997). Generally, forest vegetation dominates between 900 and 2200 m a.s.l. According to the soil map of Sicily (Fierotti et al. 1988), there is a high variety of soil types present on Mount Etna. Andosols can be found all over the mountain, often with vitric character and containing charcoal in varying amounts (Dazzi 2007; Egli et al. 2012).

The Mediterranean climate on Mt Etna is characterised by a strong contrast in rainfall between summer and winter. Nearly all the water is precipitated during the winter season, which makes conditions during the summer very dry, mainly at lower altitudes. Besides the predominant Mediterranean weather, a whole sequence of climate zones is present at the volcano which ends in alpine climate at high altitudes. Generally, the amount of rainfall is increasing with higher elevation. Mean annual precipitation is around 600-700 mm at low altitudes and 1300-1500 mm towards the summit (Ferrara 1975).

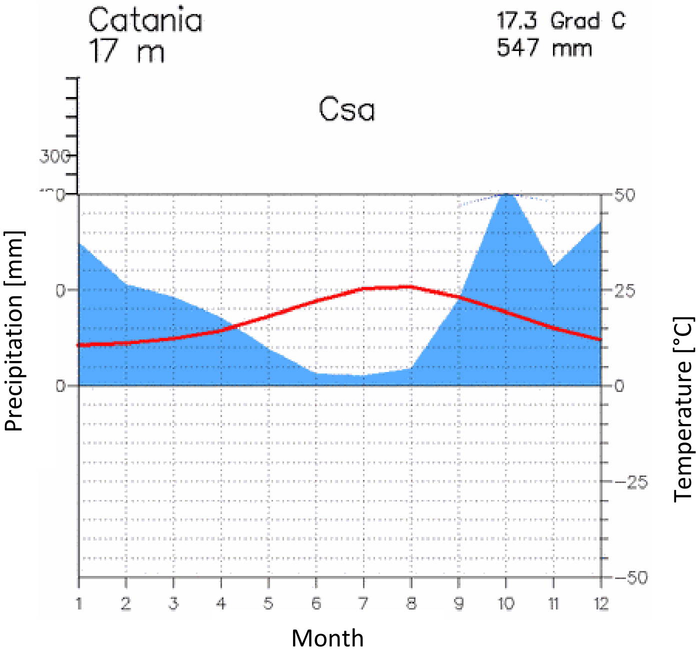


Figure 4: Climatic diagram for the city of Catania.
Values for precipitation are generally higher at the slopes of Mount Etna, whereas temperatures are usually lower (modified after Mühr, 2002).

2.1.2. Soil Profile

The general soil type, which was obtained in the field was an Andosol. Although properties changed from profile to profile, a general scheme was always found (figure 5). Very characteristic for all soils were tephra layers, on one hand lying on the surface of the soil and on the other hand intercepting the B-horizon. Data obtained from the soils is additionally given in Appendix A.

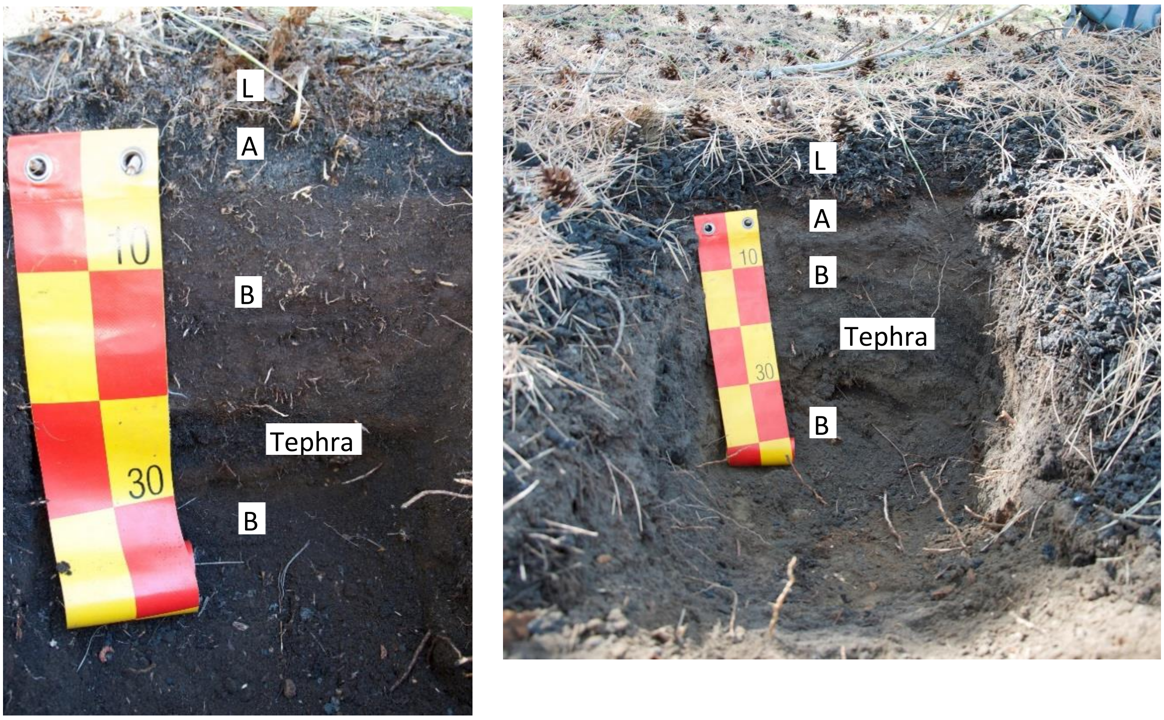
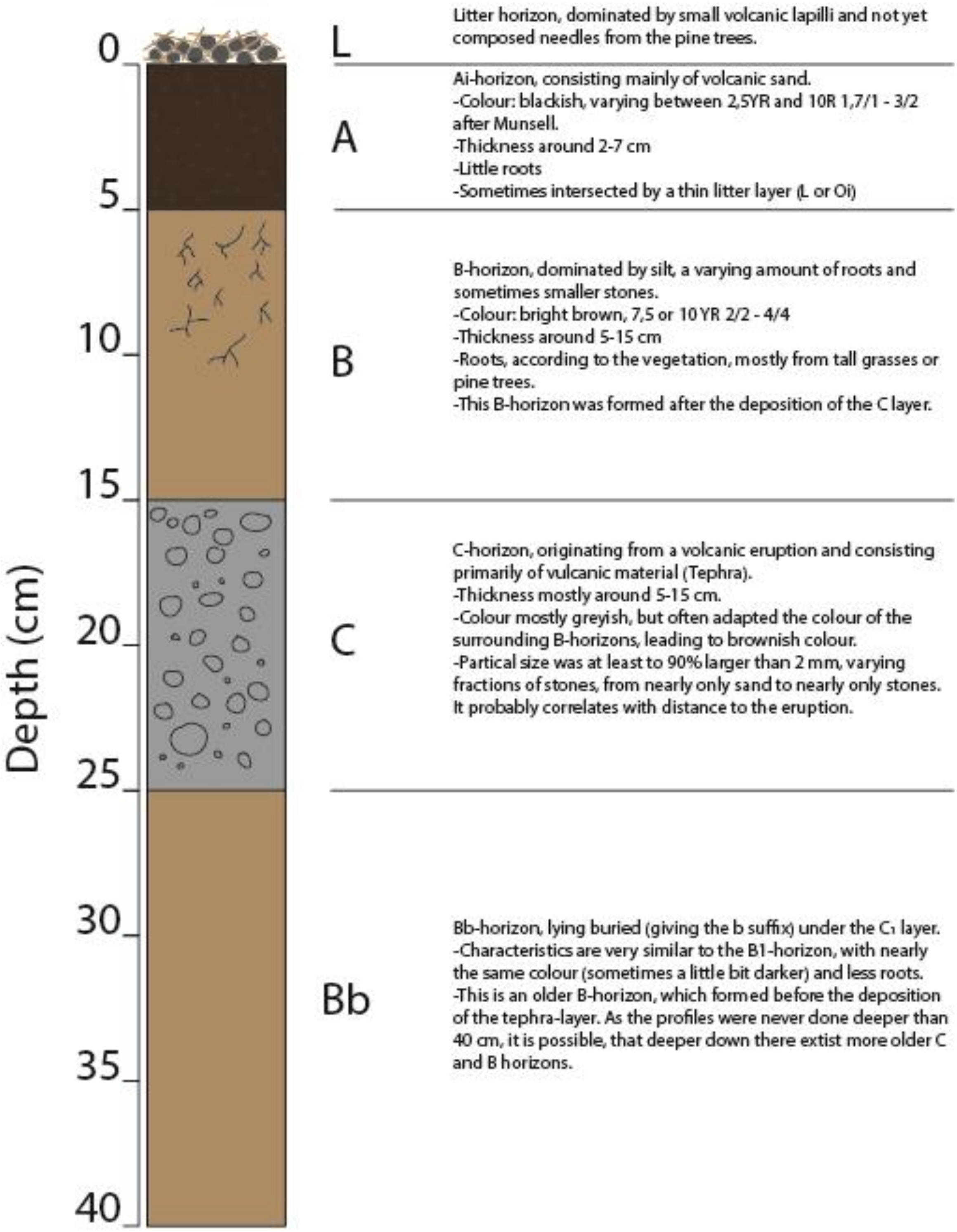


Figure 5: Soil profiles for two sampling sites.
Left: M N002; right: C 01/02_1. ***L*** *= Litter;* ***A*** *= topsoil;* ***B*** *= subsoil.*



Litter horizon, dominated by small volcanic lapilli and not yet composed needles from the pine trees.

Ai-horizon, consisting mainly of volcanic sand.
-Colour: blackish, varying between 2,5YR and 10R 1,7/1 - 3/2 after Munsell.
-Thickness around 2-7 cm
-Little roots
-Sometimes intersected by a thin litter layer (L or Oi)

B-horizon, dominated by silt, a varying amount of roots and sometimes smaller stones.
-Colour: bright brown, 7,5 or 10 YR 2/2 - 4/4
-Thickness around 5-15 cm
-Roots, according to the vegetation, mostly from tall grasses or pine trees.
-This B-horizon was formed after the deposition of the C layer.

C-horizon, originating from a volcanic eruption and consisting primarily of vulcanic material (Tephra).
-Thickness mostly around 5-15 cm.
-Colour mostly greyish, but often adapted the colour of the surrounding B-horizons, leading to brownish colour.
-Partical size was at least to 90% larger than 2 mm, varying fractions of stones, from nearly only sand to nearly only stones. It probably correlates with distance to the eruption.

Bb-horizon, lying buried (giving the b suffix) under the C_1 layer.
-Characteristics are very similar to the B1-horizon, with nearly the same colour (sometimes a little bit darker) and less roots.
-This is an older B-horizon, which formed before the deposition of the tephra-layer. As the profiles were never done deeper than 40 cm, it is possible, that deeper down there extist more older C and B horizons.

Figure 6: General soil profile which was observed at the study site.

2.2. Experimental Design

As in a previous study, the rings of the trees standing close to the line with enhanced NDVI (all trees on the line died at the eruption), were investigated and differences could be measured, this thesis relates its study design mostly on that data (Seiler et al., in progress). The trees, where the ring width was measured to be higher than for the other trees previous to the eruption (these are called "magic" trees henceforth), were chosen and there the soil was sampled. For control measurements, soil was sampled at the sites,

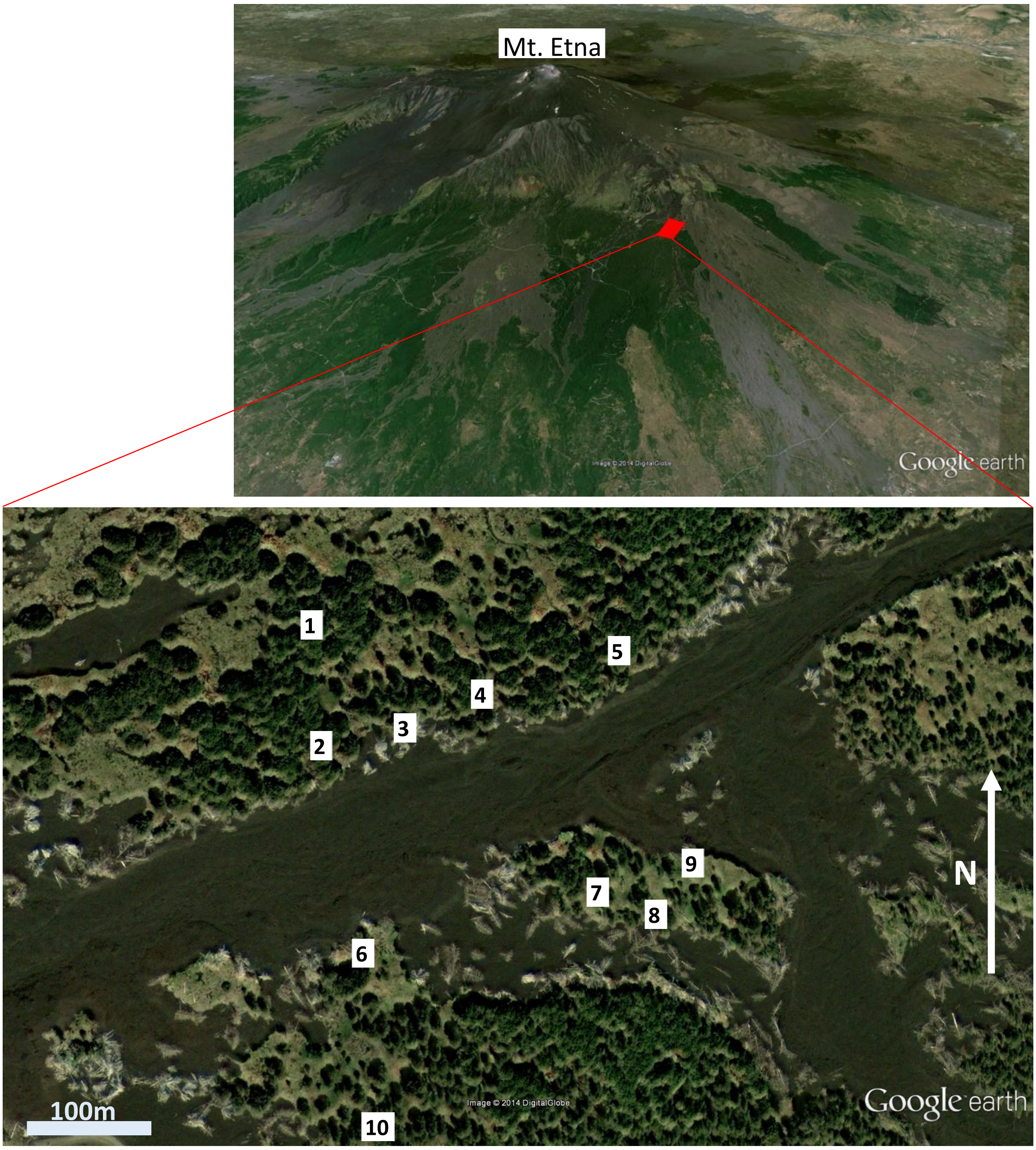


Figure 7: Sampling sites at Mount Etna.
*Magic: **1**: P013; **2**: N027; **3**: N002; **4**: N022; **5**: S006; **6**: P007; **7**: N016; **8**: N017; **9**: N013; **10**: P002; Control: **A**: C06/07; **B**: C01/02; **C**: C08/09 (Google).*

where the control trees for the tree-ring study stood. This sampling design should maximize the comparability of this dataset and the one obtained by Seiler et al.

In summary, ten sites were sampled at magic trees, and ten soils at three sites at the control trees. All sites lied on an altitude of roughly 1800 m a.s.l. On each site cores with an exact volume of 100 cm^{-3} were taken from three different depths, namely 0-5 cm, 10-15 cm and 20-25 cm. These depths were interpolated to 0-10 cm, 10-20 cm and 20-30 cm, respectively. For every depth three replicates were taken. Thus in the end there were 180 soil samples obtained ($20\ sites \times 3\ depths\ \times\ 3\ replicates$). After the bulk dry density measurements, the replicates were mixed, so that the rest of the analyses were conducted with 60 samples. Measured data was then evaluated statistically for differences between magic and control trees.

2.3. Laboratory Analysis

2.3.1. Bulk Dry Density

The bulk dry density (BDD) is defined as the mass soil per volume without any water in the pores. It is a very basic and important variable, because it is on one hand inversely proportional related to the available pore space, which is crucial for plant growth, on the other hand it is a necessary value to calculate properties relative to a surface or a volume and not only per weight (Buckman and Brady 1960; Buurman et al. 1996).

To determine the BDD of soils it is very useful to use a predefined volume for sampling. In the field a cylinder was used with an exact volume of 100 cm^3. With this it is very easy to calculate the BDD by weighing the dry soil and divide it by this 100 cm^3 to get the classically used BDD unit of g cm^{-3} or kg dm^{-3} (which is the same value).

To dry the soils, they were put in an oven for around 16 hours at 40 degrees Celsius. With this procedure, the organic substances are not getting destroyed or heavily altered, on the other hand water is evaporating very easily.

After drying and weighing, the soils were sieved with a 2 mm sieve to separate the stones (skeleton) from the so called fine earth. Stone or skeleton was weighed separately again to have the relative amount of stones in the soil.

2.3.2. pH

The pH is an indicator for the acidity or basicity of an aqueous solution (Bates 1973; Sørensen 1909). Values below 7 are considered as acidic, whereas values above 7 are considered basic. The pH influences strongly the availability of certain nutrients and is therefore a crucial property to measure whenever soil is investigated.

The pH was measured with a pH meter in a 0.01 M $CaCl_2$ solution. The soil to solution ratio was 1:2.5. An electrolytic substance like $CaCl_2$ is used, because it can decrease problems with diffusion potentials (it is also well possible to use other chemicals like KCl etc.). The pH sensor measures the resistance of this solution and can derive the pH through calibration with standardized solutions. For this calibration, two solutions with a pH of 7 and 4, respectively, were used. The process was as following:

First 20 g fine earth was weighed into a beaker, 50 ml $CaCl_2$ solution was added and the solution was mixed during 30 minutes. Then the pH was determined with the pH meter.

2.3.3. CHN

CHN stands for the elements carbon (C), hydrogen (H) and nitrogen (N) which are essential for all life on earth. With the relative or absolute amounts of these elements one can derive the total organic matter in a material, as well as some additional information like organic matter quality, which greatly depends on the ratio of C and N.

Soil samples were measured for CHN in Waedenswil ZH at the ZHAW (Zuercher Hochschule für angewandte Wissenschaften) with a TrueSpec CHN Macro Analyser (LECO Corporation, USA). 1 g of each soil sample was weighed into tin caps. These caps were carefully closed and put into the analyser. There they are first cleaned from atmospheric gases and then fall into a furnace with a temperature of 950°C. The flooding with pure oxygen leads to a fast and complete combustion into CO_2, H_2O and NO_X. CO_2 and H_2O are measured in separate cells with infrared sensors, adjusted to a characteristic absorption wavelength of the respective gas. From the amount of the gas one can derive the original solid amount.

To measure nitrogen, the gas has first to flow through a copper conduct where the oxygen is removed from the NO_X molecules and nitrogen remains as N_2. This N_2 is then cleaned from H_2O and CO_2, lead into a separate chamber and measured with a sensor for thermo conductivity.

2.3.4. Nitrate and Ammonium

Nitrate (NO_3^-) and ammonium (NH_4^+) are the most important forms in which nitrogen appears in the soil. Usually, plants cannot take up pure nitrogen (N_2) from the atmosphere but the mineral forms NO_3^- and NH_4^+, which are formed mainly by bacteria or fungi from N_2 (nitrogen fixation) or NH_4^+ (nitrification) (Winogradsky 1892).

The measurement of these two compounds was conducted with a photometric method (Alef 1991). First, 20 g fine earth was mixed with 80 ml of a 1 % K_2SO_4 solution and mixed for around 90 minutes. It was filtered with nitrate free filters into plastic bottles. This extract was used for NO_3^- as well as for NH_4^+. Like for all chemical analyses a blank specimen was also made for all steps in the process to correct for possible contamination and systematic errors during the laboratory work (also used for methods in 2.3.3. – 2.3.6). For the colour reactions flash tests were used (Machery-Nagel, Switzerland). 10 ml of the extract for the nitrate and 5 ml for the ammonium were each filled in two 25 ml volumetric flasks, which were rinsed with the K_2SO_4 solution to prevent contamination. Chemicals from the flash test were added as required and the volumetric flasks were filled up with the K_2SO_4 solution. A standard row was made with a concentration of 0, 2, 4, 6 and 10 mg L^{-1} for nitrate and with concentrations of 0, 0.2, 0.5, 0.8, and 1.6 mg L^{-1} for ammonium.

After 20 minutes the colour reaction had finished and the samples could be analysed at the photometer (Specord 40; analytikjena, Germany). The photometer measures absorption at a certain wavelength, ideally where the material of interest absorbs very strongly but other materials do not. The measured wavelength for NO_3^- was 436 nm, for NH_4^+ it was 690 nm.

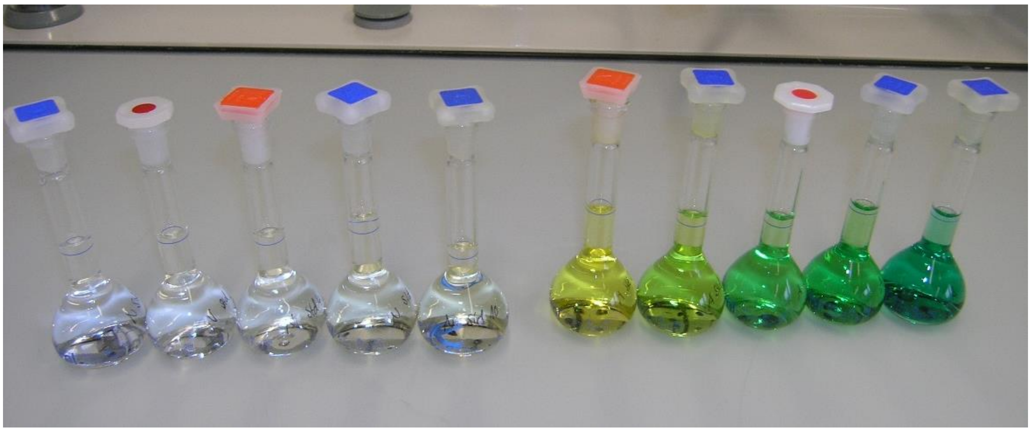


Figure 8: Standard rows for colour measurements.
Left: nitrate; right ammonium. Concentrations are increasing from left to right.

2.3.5. Phosphorus

Phosphorus (P) is one of the most important and needed nutrients for plants. As the metabolism of every higher life form on earth is based on the use of ATP (Adenosine triphosphat), which in fact has three P atoms incorporated in the molecule, it seems obvious that P is crucial for growing and sustaining life and is often a limiting factor in various environments.

In soils, P usually exists in two forms, either in soluble form as phosphate (PO_4^{3-}) or incorporated in the living or dead biomass in many different organic components. In any case all P is finally measured in the form of PO_4^{3-}.

Phosphorus was measured in three different ways. First, the entire extractable P in the sample. This total P can be divided into organic and inorganic P. The latter could be measured by heating the samples for 2h hours at 550°C in a muffle furnace, thus removing all organic compounds. Organic P was derived by subtracting inorganic P from the total P. The first two methods were done using a sulphuric acid (H_2SO_4) extraction (Kuo 1996).

The third measurement was done with an EDTA (ethylenediaminetetraacetic acid) extraction, which was also used for potassium (see 2.3.6), to obtain the plant-available part (Lakanen and Erviö 1971).

For the H_2SO_4 extraction 1 g of soil, either fresh or burnt, was mixed with 50 ml 0.5 M H_2SO_4 solution and shaken for at least 10 hours. For the EDTA extraction the relation was 10 g of soil and 100 ml of solution (0.5 M NH_4OAc + 0.02 M EDTA) and it was shaken 90 minutes.

After extraction, the process was in all three ways basically the same. First, the samples were filtered into plastic bottles before they were filled into volumetric flasks using a dilution relation with deionized water, which varied between the three extractions. The H_2SO_4 extract was diluted 10 times, whereas the EDTA extract was only diluted with a factor of 2.5.

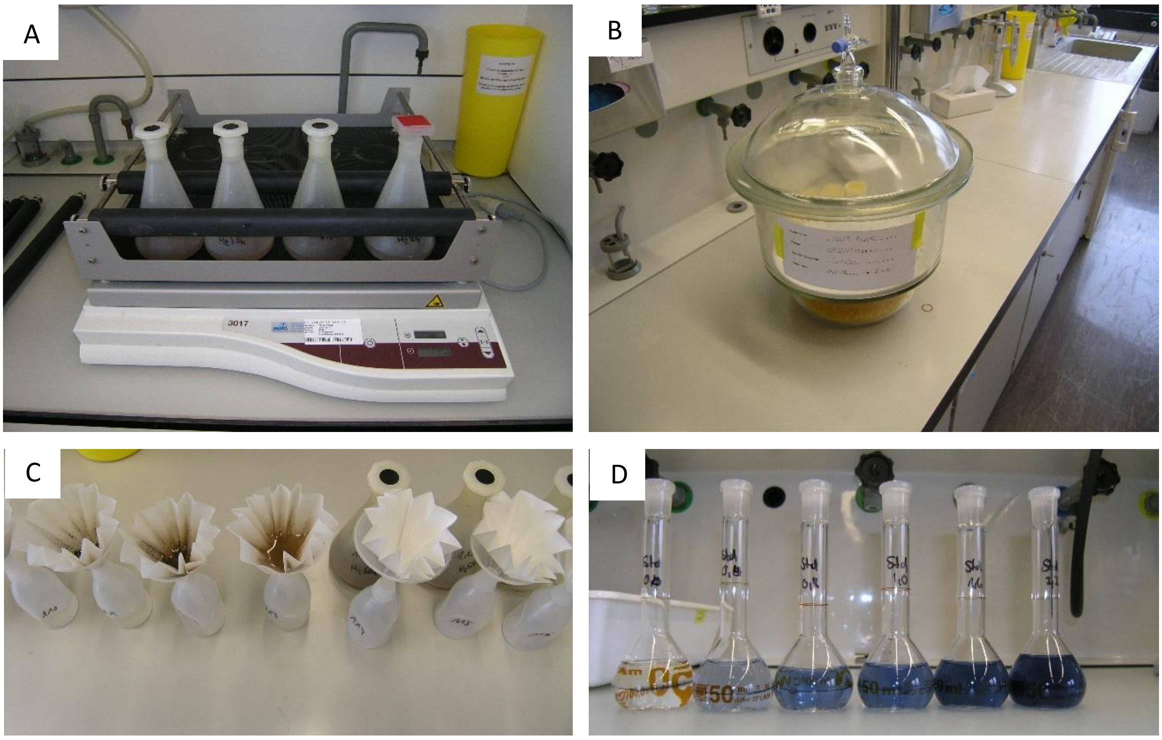


Figure 9: Methods and tools for the phosphorus measurements.
***A**: Shaking device; **B**: Incubator for the muffled samples; **C**: filtrating process; **D**: standard row after colour reaction.*

The colour reaction was induced using several chemicals. First, some drops of p-nitrophenol indicator were added, then drop by drop a 5 M NaOH solution until the colour changed to yellow (which indicates that the solution is basic). Dropwise addition of 0.5 M H_2SO_4 until the colour changed back to transparent made sure the solution was in the correct pH range of around 2.2-2.5 for the final colour reaction. It was induced by adding 8 ml of a solution of 5.3 g L^{-1} ascorbic acid (vitamin C), 6 g L^{-1} ammonium heptamolybdate, 73 mg L^{-1} antimony potassium tartrate and 74 ml L^{-1} conc. H_2SO_4. Phosphate falls out with the molybdate as a salt, creating a blue suspension. This was measured at the photometer using a wavelength of 880 nm after waiting at least 1 hour during which the colour reaction finished completely.

2.3.6. Potassium

Potassium (K) is another very important nutrient element. As potassium silicates, like feldspar, are very difficult to digest, there can be a lack of this element in soils. K plays an important role in osmosis, increasing the turgor and many metabolism processes and is therefore crucial for the plant to survive (Mengel 1961).

For the K analysis the same EDTA extract as for the plant available P was used. Thus, the measured K is only showing the part of K in the soil which is accessible for the plants. In contrast to phosphorus, K was not measured at a photometer, but using an atom absorption spectrometer (AAS; PerkinElmer Inc., USA). In an AAS, the solution is completely burnt with a mixture of acetylene (C_2H_2) and oxygen. The flame shows always characteristic absorption features of the elements which are burnt. A lamp with the same wavelength as the combustion colour of potassium sends light through the flame. A sensor on the other side of the flame measures the incoming radiation and, by comparing it to a calibrated standard, can calculate the relative amount of K in a solution.

Extracts were diluted and drawn into the machine with a small plastic tube. The AAS measured automatically three times and calculated mean and standard deviation of every single sample. Calibration with a standard row was made every fifteen samples.

2.4. Statistical Analysis

Whenever normality of the dataset could be assumed, a two way ANOVA was carried out, inferring that the data is a function of the group and of the depth. Mathematically spoken:

$$data = f(group\ x\ depth)$$

Whenever it was not possible to assume that the sampling distribution was normally distributed, a non-parametric Man-Whitney-U rank sum test was used. This could only test if control and magic group differed significantly from each other.

All statistical tests were run with Sigmaplot12.0 (Systat Software GmbH, Germany). A more complete insight in the statistical analysis is given in Appendix B.

Additionally, a principle component analysis (PCA) was conducted with SPSS (IBM, USA), to see if the entity of analysed variables gives the possibility to see a difference between magic and control groups.

3. Results

All results are generally given in weight per volume, except pH, which has no unit, and CHN, which is commonly given in per cent by weight.

Note that the common unit for K, NO_3^-, NH_4^+ and available P is µg cm^{-3} which is equivalent to mg dm^{-3} and g m^{-3}. The unit of organic and total P is given as mg cm^{-3} and equivalent to g dm^{-3} or kg m^{-3}.

3.1. General description of the sampled soils

The samples were generally less dense than 1 g cm^{-3}, which can be expected from volcanic soils. Grain size mostly varied between sandy and silty (see figure 6). The pH slightly decreased in most cases with depth from around 4.9 in the topsoil to around 5.1 in the subsoil. Organic matter (represented by the total carbon) was the highest in the uppermost 5 to 10 cm and decreased with depth. All other nutrients were in average most abundant in the uppermost layer, as well.

The requirements for the andic property are not perfectly met, as the BDD is mostly slightly higher than 0.9 g cm^{-3}. On the other hand, the prerequisites to be vitric seem to be fulfilled. There is a considerable amount of volcanic glass in the fine earth fraction, which definitely exceeds 5 %. The organic carbon content is always lower than 5 % and the phosphate retention capacity is very high, when comparing total and available phosphorus (table 1). The amount of aluminium and iron was not determined, therefore it cannot definitely be concluded, that the soil has vitric properties. However, the probability of finding more than 0.4 % of aluminium and iron in a soil containing so much volcanic glass seems very high.

To conclude, the sampled soils can be determined as vitric Andosols. Most importantly, this stays the same for both groups, magic and control. Further information about the soil profiles of every site are given in Appendix A.

Magic soils

	BDD [g cm-3]	pH	C [%]	P tot [mg cm-3]	P org [mg cm-3	P av [µg/cm3	NH4 [µg/cm3]	NO3 [µg/cm3]	K [µg/cm3]
Mean	0.97	4.98	1.81	0.77	0.12	2.57	3.56	22.75	17.79
0-10 cm	0.89	4.86	3.84	0.69	0.10	4.09	5.03	35.58	24.26
10-20 cm	1.01	4.96	1.69	0.80	0.15	2.24	3.11	18.20	14.60
20-30 cm	1.00	5.12	1.12	0.83	0.12	1.38	2.55	14.48	14.50

Control soils

	BDD [g cm-3]	pH	C [%]	P tot [mg cm-3]	P org [mg cm-3	P av [µg/cm3	NH4 [µg/cm3]	NO3 [µg/cm3]	K [µg/cm3]
Mean	0.92	5.10	2.30	0.77	0.07	2.13	3.14	22.44	21.22
0-10 cm	0.88	4.94	3.68	0.67	0.06	2.70	4.03	36.32	26.82
10-20 cm	0.94	5.10	1.08	0.68	0.08	2.22	2.40	18.19	15.58
20-30 cm	0.93	5.26	2.13	0.82	0.07	1.48	3.00	18.82	21.27

Table 1: Overview of the measured variables.

3.2. Bulk Dry Density

Statistical analysis of BDD revealed no significant difference between control and magic trees. Descriptive statistics give a first impression of the measured data. The mean for the groups includes always all samples independent of depth. The mean for the depth includes always all samples from this distinct depth, independent of group. This remains the same for all investigated properties and reflects the ANOVA analyses, where the two factors are group and depth.

Here all values are given in g cm^{-3}:

Group	**Mean**	**Stdv.**		**Depth**	**Mean**	**Stdv.**
Magic	0.967	0.214		0-10 cm	0.884	0.220
Control	0.915	0.142		10-20 cm	0.974	0.160
				20-30 cm	0.965	0.155

Table 2: Descriptive Statistics of the BDD.

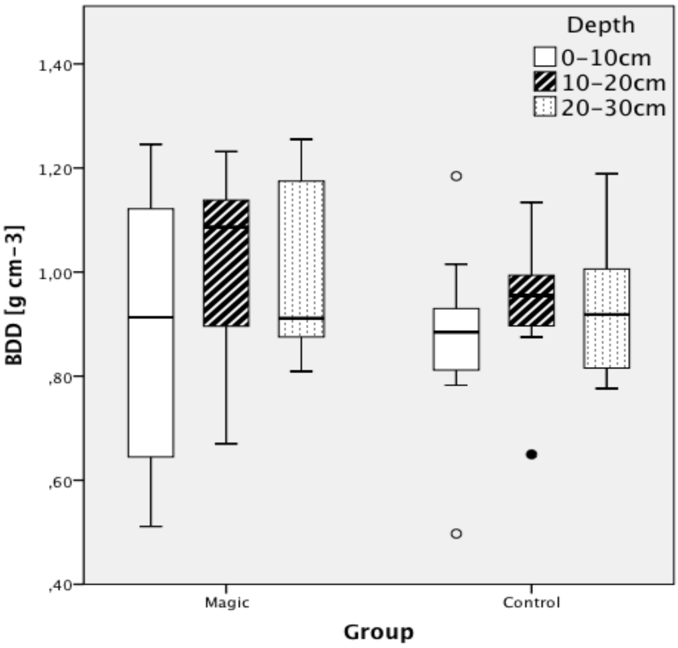


Figure 10: Boxplot, showing the data for the bulk dry density.

An ANOVA was carried out and gave *p*-values of 0.273 and 0.242 for group and depth, respectively. The interaction between group and depth was not significant here either, nor in any analyses henceforth. Therefore it will not be discussed (*p*-values for the interactions are given in Appendix B). These values indicate that the difference in mean is not large enough to rule out the possibility that it was just due to sampling or in field variability of this property.

3.3. pH

The pH in fact showed a significant difference between magic and control group. Although difference between the means was very small, the *p*-value fell below the significance level of 0.05. Measurement and analysis gave the following values for groups and depth:

Group	**Mean**	**Stdv.**		**Depth**	**Mean**	**Stdv.**
Magic	4.978	0.261		0-10 cm	4.899	0.229
Control	5.098	0.233		10-20 cm	5.028	0.234
				20-30 cm	5.188	0.220

Table 3: Descriptive Statistics of the pH.

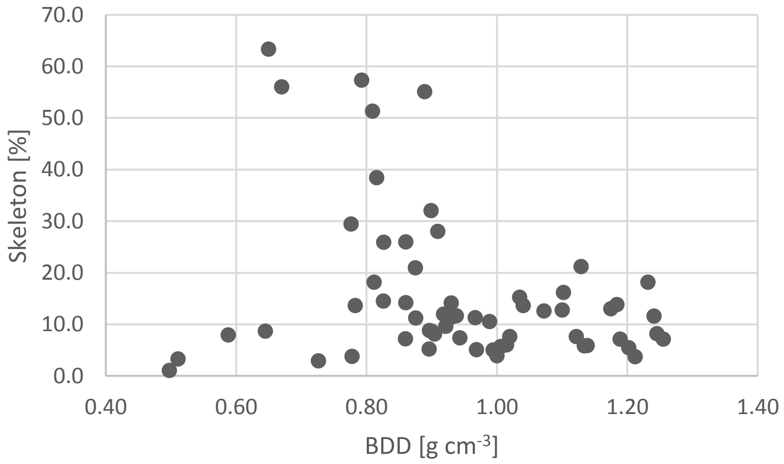


Figure 11: Correlation between the amount of stones and the BDD.
Stones = particles >2mm, given in weight %. The uppermost values for skeleton content probably result from hitting the tephra layer when sampling. Generally, left hand points can be attributed more to the topsoil, whereas subsoil samples lie mostly on the right side.

The ANOVA delivered *p*-values of 0.043 and <0.001 for group and depth, respectively. In both cases the values are below the significance level of 0.5, which indicates that the difference in the mean is not due to sampling and analysis variability but reflects a true difference occurring in the field. Thus, the two groups differ significantly when looking at the first 30 cm as a whole. Furthermore, there is a clear gradient for depth, independent of the group.

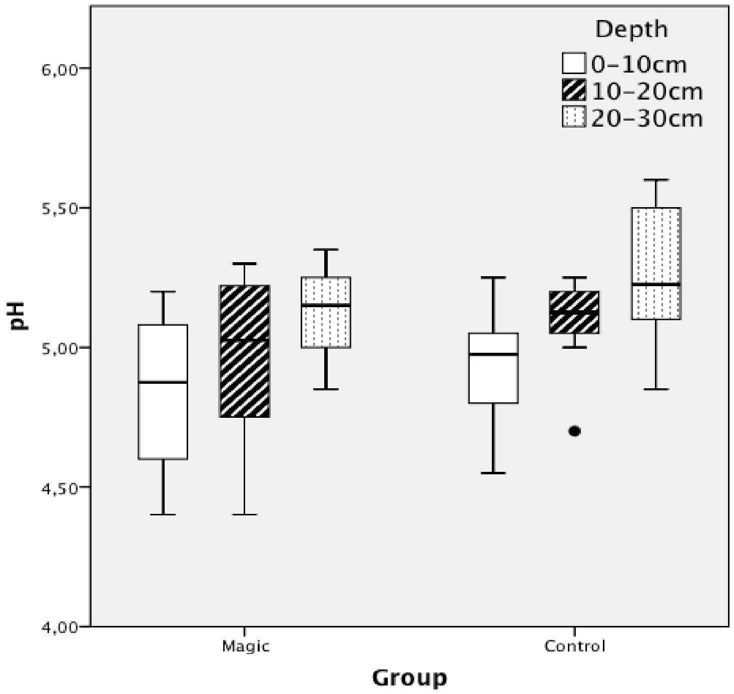


Figure 12: Boxplot of measured pH.

3.4. CHN

3.4.1. Total Carbon

Abundance of carbon was in most samples rather low, such that it was often not possible to detect it properly with the available instrument. Nevertheless, some statistical analyses offered interesting results (values are given in weight per cent):

Group	Mean	Stdv.		Depth	Mean	Stdv.
Magic	1.807	2.418		0-10 cm	3.566	2.717
Control	2.298	2.082		10-20 cm	1.134	1.166
				20-30 cm	1.456	1.540

Table 4: Descriptive Statistics of measured C.

Because the data was not normally distributed, a Man-Whitney-U test was conducted. It resulted in a *p*-value of 0.047. This *p*-value indicates, that there is indeed a difference between the groups in the first 30 cm which is bigger than what can be expected from variability induced by nature, sampling process and analysis.

3.4.2. Total Hydrogen

The amount of hydrogen in the samples was easier to detect than the amount of carbon. This makes analysis more reliable. Values are again given in weight per cent. Because a hydrogen atom is around twelve times lighter than a carbon atom, one would need to correct for molar weight when calculating a C to H ratio or something similar.

Group	Mean	Stdv.		Depth	Mean	Stdv.
Magic	0.135	0.166		0-10 cm	0.234	0.222
Control	0.144	0.148		10-20 cm	0.079	0.076
				20-30 cm	0.106	0.081

Table 5: Descriptive Statistics of measured H.

An ANOVA resulted in a *p*-value of 0.004 and 0.153 for depth and group, respectively. This indicates that the amount of hydrogen differs significantly with depth, independent of the group, whereas the difference between the groups was not big enough to make sure it was not due to sampling and natural variability.

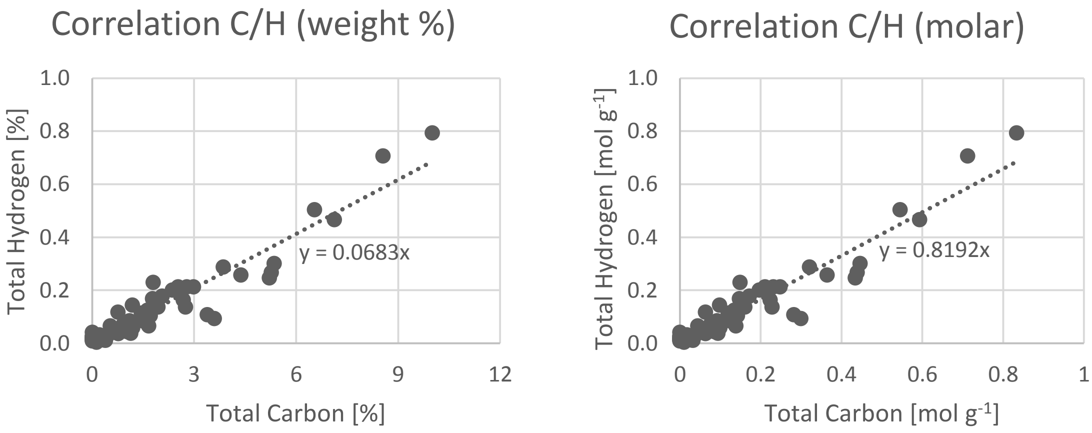


Figure 13: Correlation between the amount of Carbon and Hydrogen in the samples.
Correlation coefficient for these two variables is 0.95. The H/C ratio (molar) is nearly 1 with 0.82.

3.4.3. Total Nitrogen

Unfortunately, the nitrogen concentration was so low, that it was hardly possible to detect any N in the samples. Only ten out of sixty samples even showed a value, most of them being of the magic group. This was not enough to conduct a serious statistical analysis. However, the two most important nitrogen compounds in the soil, nitrate and ammonium, have lower detection limits and are discussed below.

3.5. Nitrate and Ammonium

3.5.1. Nitrate

The descriptive statistic of measured NO_3^{2-} is given is given hereby in µg cm^{-3}:

Group	Mean	Stdv.		Depth	Mean	Stdv.
Magic	22.754	18.539		0-10 cm	35.949	20.376
Control	22.443	12.984		10-20 cm	18.197	8.581
				20-30 cm	16.649	7.299

Table 6: Descriptive Statistics of measured nitrate.

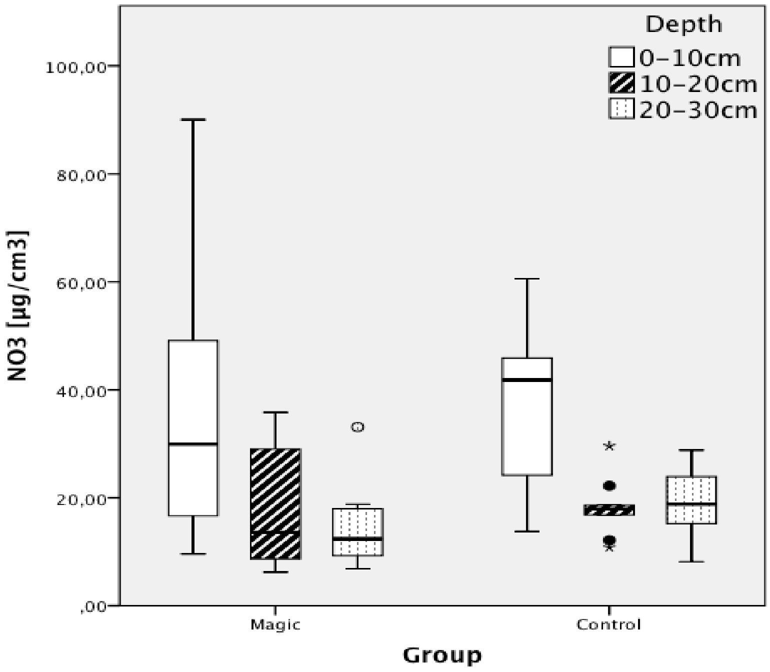


Figure 14: Boxplot of the measured nitrate values.

A Man-Whitney-U test yielded a *p*-value of 0.158, meaning that the difference between control and magic group was not big enough to rule out the possibility that it originated from natural or sampling variability.

3.5.2. Ammonium

Ammonium is around six to seven times less abundant in the soils than nitrate. Values are given in µg cm^{-3}, the same unit as for nitrate.

Group	Mean	Stdv.		Depth	Mean	Stdv.
Magic	3.563	2.697		0-10 cm	4.529	2.447
Control	3.142	1.209		10-20 cm	2.755	1.892
				20-30 cm	2.774	1.313

Table 7: Descriptive Statistics of measured ammonium.

The ANOVA, which was run with a log-transformed dataset to achieve a normal distribution, resulted in *p*-values of 0.528 and 0.015 for group and depth, respectively. This indicates that the concentration of NH_4 strongly correlates with depth, independent of the group, but does not show a significant difference between the two groups.

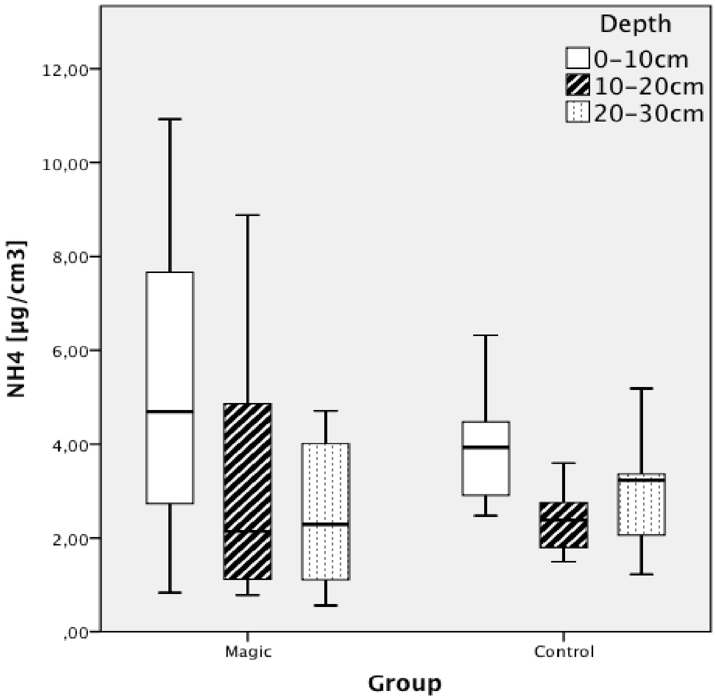


Figure 15: Boxplot of the measured ammonium concentrations.

3.6. Phosphorus

Phosphorus is divided into total P, organic P and available P. A descriptive statistic of this data is given below.

Total P [mg cm^{-3}]						
Group	**Mean**	**Stdv.**		**Depth**	**Mean**	**Stdv.**
Magic	0.774	0.270		0-10 cm	0.676	0.200
Control	0.722	0.246		10-20 cm	0.743	0.217
				20-30 cm	0.825	0.327
Organic P [mg cm^{-3}]						
Magic	0.122	0.121		0-10 cm	0.080	0.107
Control	0.070	0.078		10-20 cm	0.112	0.112
				20-30 cm	0.096	0.096
Plant-available P [µg cm^{-3}]						
Magic	2.567	2.240		0-10 cm	3.392	2.230
Control	2.134	1.139		10-20 cm	2.230	1.503
				20-30 cm	1.429	0.707

Table 8: Descriptive Statistics of measured P.

Total phosphorus is in average six to ten times more abundant than the organic phosphorus which is incorporated in living or dead biomass. The plant-available phosphorus is only a very small part of the whole P in the ground and accounts in average for hardly even 1 %. Inorganic P, which is basically total P minus organic P, is in all cases much larger than the organic part, meaning that most of the P is incorporated in the minerals, chemically bound or adsorbed to mineral surfaces.

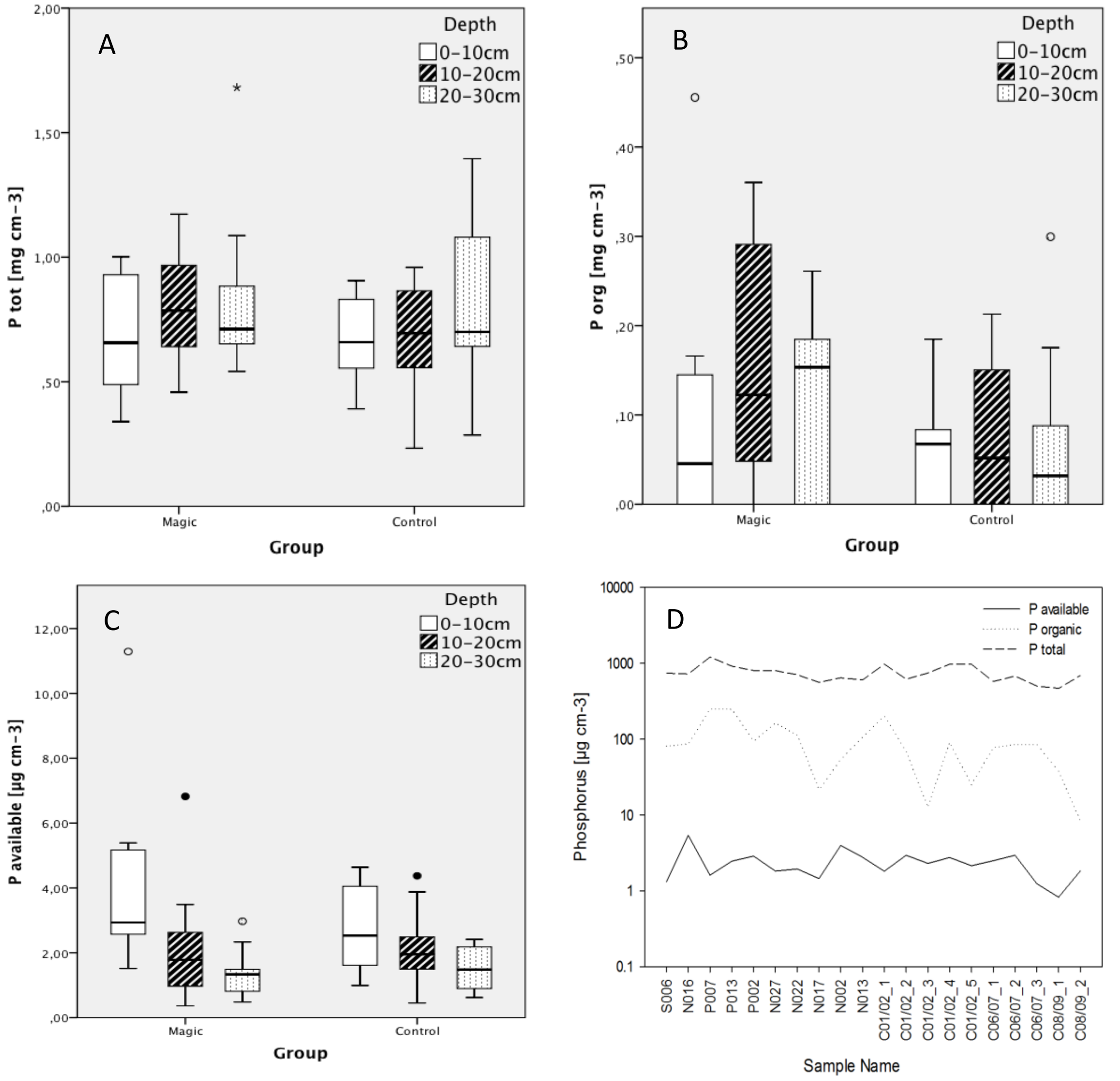


Figure 16: Graphical representation of measured phosphorus.
***A**: boxplots for the total P data. Mean values vary less than for the other P data. **B**: boxplots for the organic P. As these are approximated values, also amounts of zero mg cm^{-3} occurred, which explains that the boxes are mostly limited by the x-axis at 0.0. **C**: boxplots for the plant-available P, measured with an EDTA extraction. **D**: Combined data of all P measurements on a logarithmic scale. The first ten samples are from the "magic" trees, the second half is control.*

An ANOVA was carried out for total and plant-available P. Total P neither differed significantly with depth, nor between the two groups, with *p*-values of 0.199 and 0.444. Plant-available P is very strongly dependent from depth, in all groups, with a *p*-value of <0.001. But has no large enough difference between the two groups to exclude the possibility that it originated from random natural variability (*p*-value = 0.768). Organic Phosphorus was, with a *p*-value of 0.139 at the Man-Whitney-U test, not significant.

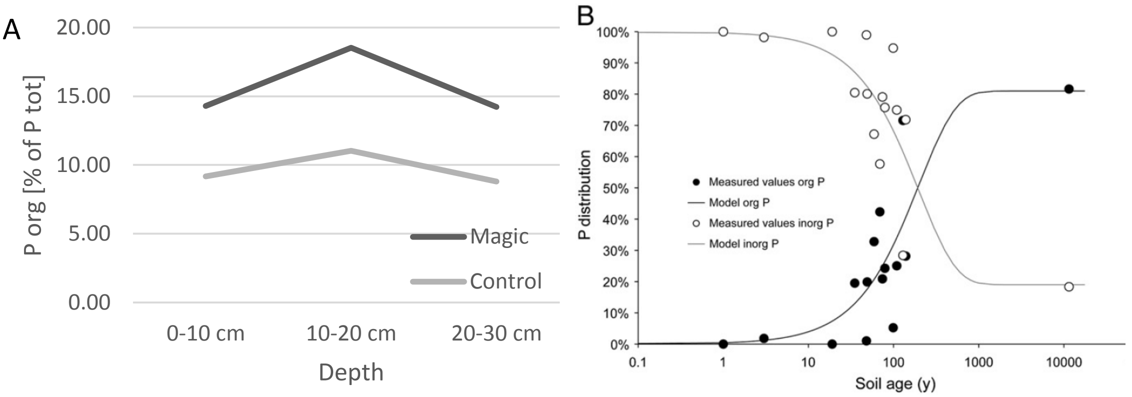


Figure 17: Relative amount of organic P and age determination.
***A**: Measured relative amount of organic P for magic and control soil. **B**: Relation between the relative amount of organic P and the soil age in a glacier forefield (Egli et al. 2012).*

According to Egli et al. (2012) the age of a soil can be estimated by the relative amount of organic phosphorus, compared to the inorganic part. With approximately 10-15% organic P the soil would be between 10 and 100 years old (figure 17).

3.7. Potassium

The plant available potassium, measured with the EDTA extract, gives mean values between 15 and 25 µg cm^{-3}. In average, the amount of K is higher in the control than in the magic group.

Descriptive statistics are given in µg cm^{-3}:

Group	Mean	Stdv.		Depth	Mean	Stdv.
Magic	17.786	9.494		0-10 cm	25.542	6.383
Control	21.224	9.321		10-20 cm	15.091	9.014
				20-30 cm	17.883	9.793

Table 9: Descriptive Statistics of measured K.

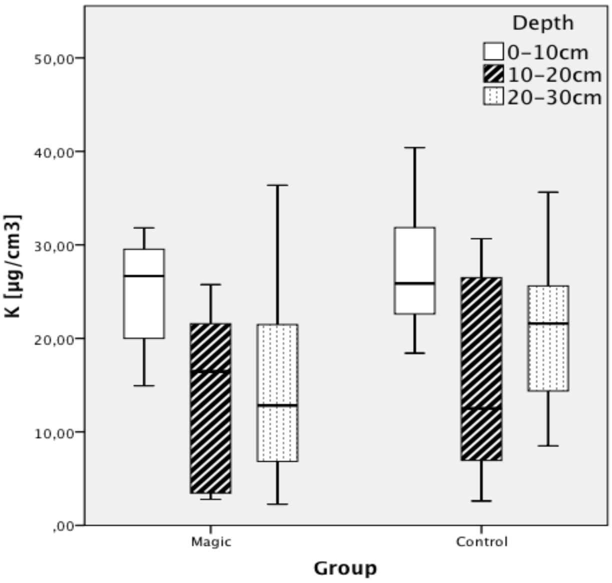


Figure 18: Boxplots of the measured plant available potassium.

An ANOVA revealed *p*-values of 0.122 and <0.001 for group and depth, respectively. A strong correlation between K and depth of all samples exists, which is significantly higher than the variability expected in nature. The *p*-value for group on the other hand, suggests that the difference between the means of the two groups for the first 30 cm in the soil is not significantly larger than the natural variability from sampling and in field variation.

3.8. Principle Component Analysis

When applying a PCA, the input variables are linearly combined to produce so called principle components, which explain as much variance as possible in a dataset (Pearson 1901). Usually, one can use the first two or three components, which explain the most variance and calculate on with these to be able to maximize the expressiveness of the results and minimize the noise (random variability) in the dataset. A further understanding of the mechanisms of a PCA is not necessary to understand the following results. Input variables were BDD, organic P, plant-available P, NO_3^-, NH_4^+ and K.

After the transformation into the principle components they are sorted (figure 18) and the first two are plotted against each other (figure 19). Thus the maximal amount of variance is shown in a two dimensional plot. A difference in the two groups would then result in a grouping of the data points. It was not the case in this data.

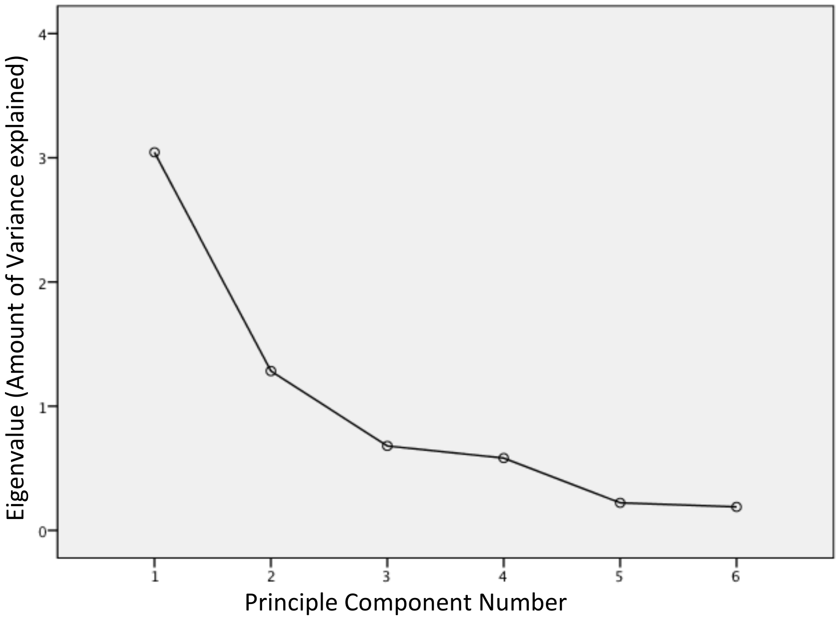


Figure 19: Principle Components, sorted for their Eigenvalue.

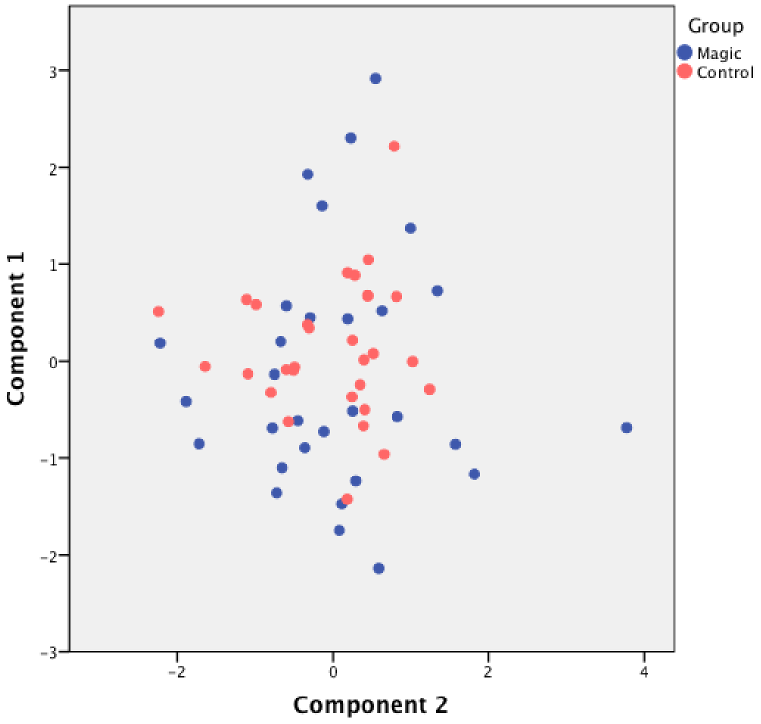


Figure 20: Magic and Control data points plotted on the two principle components.

4. Discussion

4.1. General placement of the investigated soil

The sampled soils represent rather common volcanic soils, appearing on volcanoes all over the world. The pH is very common for systems without carbonates and lies in a range, where many plants can easily grow. The values for organic carbon account for very wide spread occurring soils, even if they are not volcanic. Usually, values hardly exceed 5 % in natural ecosystems. There are of course exceptions, but these are mostly constrained to anoxic conditions (e.g. in peatlands). Potassium values are comparable to other volcanic soils, for example at Merapi (Indonesia), where the extracted K from volcanic ashes was around 39 mg kg^{-1} (Anda and Sarwani 2012). Here the values were varying around 20 mg kg^{-1}, so the amounts correspond pretty well. The phosphorus content in the investigated soil is very common as well, at least compared to natural ecosystems without fertilizer input (in agriculturally used areas the values can be much higher). The values are well in range with P concentrations measured in 32 soils in Portugal (do Carmo Horta and Torrent 2007). Regarding the amounts of ammonium and nitrate measured, it is very difficult to place them in a special soil, as mineral nitrogen pools vary a lot spatially and seasonally. Generally, high nitrate values compared to ammonium, which can be observed here, indicate that the soil is well aerated, as ammonium is in soils quickly transformed to nitrate in the presence of oxygen (Stahr et al. 2012). To sum up, the investigated soils are common for volcanic environments, in regard to the vitric properties, and do not show extraordinary or striking features, when looking at the measured variables.

4.2. BDD

Bulk dry density measurements resulted for magic as well as for control soils in values of 0.9-1 g cm^{-3}. Variation inside the magic group is much higher than inside the control group or between the two groups. A probable reason for this variation is the larger environmental differences between the magic sampling sites. There the conditions changed much more from site to site, as the respective trees were sometimes standing alone, or close together and nearer or further away from the old lava flow. In contrast, BDD has a much lower variation in the control group, resulting from only three main sites used, which were all lying in pine forests with comparable tree density. However, the average BDD is for both groups very similar, thus providing a robust comparability for the different nutrients. The values are rather low, which is not surprising on a volcanic soil of which the mineral phase is largely comprised of pyroclastic material, having a high porosity and accordingly a low density. Generally, low values can be regarded as very good for plants, because a high porosity promotes easy root growth and a high water holding capacity, but also good drainage when water input is high.

4.3. pH

The pH was next to the total carbon the only property measured with a significant difference between the two groups. However, the mean values of the groups are so close together, that an influence on the growth of the plants can hardly be explained with it. They lie both very close around 5, indicating that silicates act as buffer, increasing the availability of cations like potassium, calcium or magnesium. Reaching values under 5 can furthermore promote the dissolution of iron and aluminium oxides, which is desirable in small amounts, though the concentration of aluminium can also quickly reach a level, where it acts toxic (Stahr et al. 2012).

The values are increasing with depth. However, the gradients are in this case very small and close to the overall average, such that all soil samples can be regarded quite homogenous when it comes to pH. Factors influencing pH, like all the parent material above, but also litter input, vegetation type, precipitation and ground water level are hardly changing inside and between the two groups.

4.4. CHN

Carbon, Hydrogen and Nitrogen were measured in weight percentages. Therefore it is not surprising that many values, above all of nitrogen, are below the detection limit. Unfortunately, it was not possible to derive a C/N ratio for SOM in the soil, which would have made possible to make assumptions about the quality of the litter and the organic material. However, measured carbon and hydrogen values were more reliable. Carbon values of around 10 kg m^{-2} are expected for Andosols (Batjes 1996). The data, collected in this work results in approximately 30 kg m^{-2}. Admittedly, litter which was sampled with topsoil might have greatly biased the dataset by resulting in too high values for organic material.

It is striking, that there is indeed significantly more carbon stored in the control soils than in the magic soils. Usually, one would expect more carbon in more fertile soils. Thus this would make no sense to explain the enhanced vegetation growth which was observed. On the other hand, less carbon could also result from an enhanced decomposition rate or less litter fall. The first explanation would support a hypothesis assuming an increased temperature. It is yet very difficult to explain the difference in the total organic carbon, as it remains unclear in which form the carbon was bound. Thus it would be possible that there were much more roots at the control sites, or possibly litter contaminating the topsoil, which was certainly the case at some samples which showed values above 8 % for the first five cm. On the other hand, the mean carbon values were in every depth higher at the control soils, thus signalizing a different explanation. Regarding hydrogen the trend points in the same direction as for carbon. However, differences were not statistically significant. Nevertheless, changes are very similar to carbon, which also results in a very good correlation between carbon and hydrogen over all samples. When calibrating for molar weights, the ratio of 0.82 between C and H reveals that there are nearly as much hydrogen atoms in the sample as carbon atoms.

CHN data might give an important hint on differences in the samples but one would need much more information about litter quality and the form in which soil organic matter is present to draw conclusions out of it.

4.5. Nitrate and Ammonium

Usually the percentage of mineral nitrogen to the total nitrogen in soils is not larger than 2%. However, nitrate and ammonium are the forms in which nitrogen can be taken up by the plants and are cycled comparably quickly (Haynes 1986).

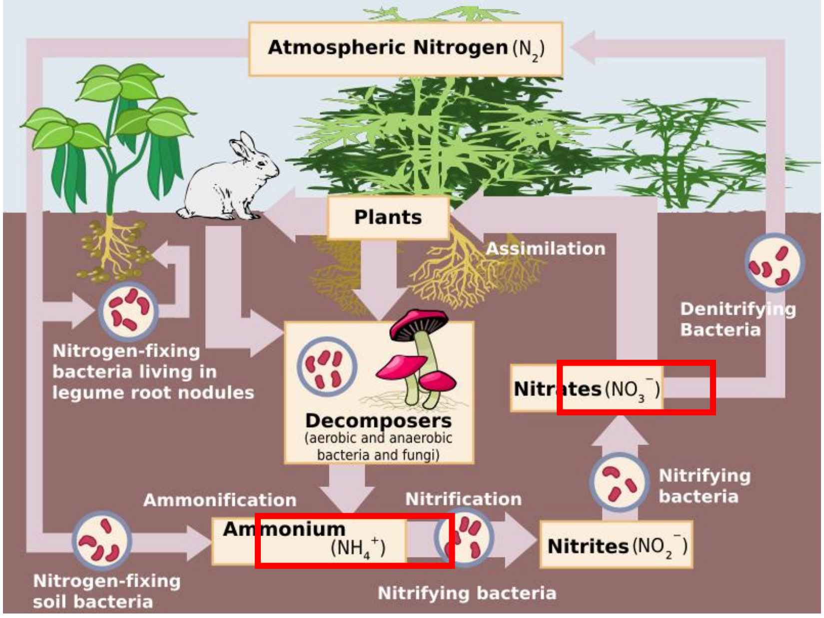


Figure 21: Schematic of the nitrogen cycle.
Nitrate and ammonium are highlighted red. Modified after Johann Dréo (2009).

Regarding the nutrition of plants, they are always constrained to the element which is in relation least accessible (Carl Sprengel 1828; Justus von Liebig 1855). Nitrogen is often a limiting factor for plant growth, which explains its massive application in fertilizers.

Consequently, an increase in mineral nitrogen might promote enhanced growth of trees. However, the amounts of NO_3^- and NH_4^+ could not be tested to be significantly different between the two groups. Thus it is unlikely that nitrogen played a major role in the enhanced tree growth. The variation of nitrogen in the soils was extremely high, making it very hard to test. The *p*-value of nitrate (0.158), however, indicates a difference, which might intensify when using more samples.

Generally, nitrogen would not be expected to be very abundant, neither in volcanic gases, nor in their fluids. This originates from the fact that nitrogen is very volatile and neither abundant in any usual rock type on the surface of earth nor in the mantle, but usually originates from the atmosphere or decomposed organic material. Thus, even if a significant difference had been found, the question of causality would not have been answered. It might be more likely that an enhanced plant growth promoted a higher abundance of mineral nitrogen. On the other hand, fixation of nitrogen, leaching of nitrate and turnover in general are processes which happen very fast compared to the time between eruption and sampling, which was after all more than ten years.

4.6. Phosphorus

In a study which took place in the Swiss Alps, concentrations of total P were mostly around 300-600 mg kg^{-1} (Egli et al. 2012), whereas in this study the mean concentration was 790 mg kg^{-1}. From this one can conclude at least that the volcanic parent material is rather enriched in P, compared to other magmatic or metamorphic rocks. However, as these concentrations are not corrected for the BDD, it is difficult to draw conclusions on the total stocks of P in such soils.

The statistical analyses showed, that none of the investigated P partitions differed significantly between the groups. Regarding plant growth organic and plant available phosphorus are probably more important to deal with. Organic phosphorus was indeed not significantly different, but the low *p*-value could indicate a difference, meaning more organic P in the magic group, which could be identified more clearly with more samples. Such a difference in organic P would indicate, that either the plants had taken and incorporated more phosphorus, or the total amount of organic matter was just higher in the magic group. Both explanations have yet substantial drawbacks. Firstly, carbon was tested to be significantly lower in the magic group than in the control group, thus making the explanation of a higher amount of organic matter in the soil meaningless. Secondly, the signal in the tree rings from the years before the eruption did not show an increase in P (figure 22). It remains unclear, whether the small and not significant differences between magic and control group are just by chance, resulted from the spatial distance between the groups or something entirely different happened.

It was stated, that in young, evolving soils inorganic P is quickly transformed into organic and plant available P (Egli et al. 2012). However, the assumption is not supported by this study, as percentage of organic P did not increase with depth (figure 17). Though the data only contains the first 30 cm which might not be meaningful overall.

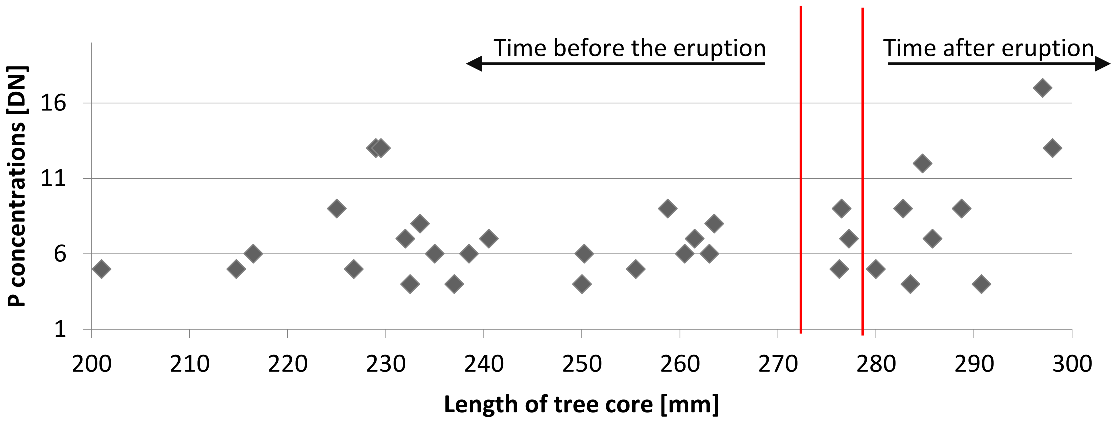


Figure 22: Concentration of Phosphorus in tree core.
In red is marked the beginning (left line) and the end (right line) of the year 2003, in which the eruption occurred (modified after Seiler 2014).

Concerning the plant available P, which is only a minor part of the total P and much smaller than the organic P, its concentration is highly dependent of the pH. In a range of around 5 (compare chapter 3.2. and 4.2.), phosphorus is strongly bound by aluminium and iron (Busman et al. 2009), explaining why there is only little available P, compared to the other pools. Furthermore, an addition of available P (through fluids or dust) in Andosols does not affect organic P, nor available P as it is thought to be sorbed quickly to the large surface area of the volcanic rocks (Meason et al. 2009). Thus, an addition of phosphorus in any form preceding the eruption would probably not have led to a strong increase in available P concentration.

4.7. Potassium

K is often a limiting factor in plant growth, as it makes up around 0.5% – 2% of the plant dry weight. It appears in nearly all volcanic and secondary rocks. However, it is difficult for the plant to dissolve mineral potassium (Greenwood and Earnshaw 1997).

K is also present in Etna’s groundwater in considerable amounts. It is thought to be dissolved when the water interacts with the volcanic rock under acidic conditions, resulting from contributions of CO_2 and SO_2 from volcanic gas (Giammanco et al. 1998). A change in available K concentrations could thus be related to a change in the groundwater and volcanic gas interaction. However, no significant difference between the groups could be found. Although the *p*-value of 0.122 is rather low and might indicate a difference which could be better detectable with more samples, its variation is very high inside the groups. Furthermore, the values for the control group are in average higher than for the magic group. This seems counterintuitive when thinking about the enhanced growth. Therefore, the causal relationship between the difference in the K concentration and the difference in tree growth must be strongly doubted. A possible reason for the measured differences has rather to be attributed to the general spatial distance and heterogeneity in soils.

As can be seen in figure 23, the amount of K in the plant varies in a slowly oscillating way. It remains unclear, whether this is due to the plant itself or environmental factors. The concentration of K are increasing in the years 2002 and 2003, which would be a nice correlation with the enhanced tree growth. However, the rise in K does not stop and even reaches a maximum some years later. The samples, reflecting the soil ten years later might therefore be strongly biased by this strong increase in the K signal.

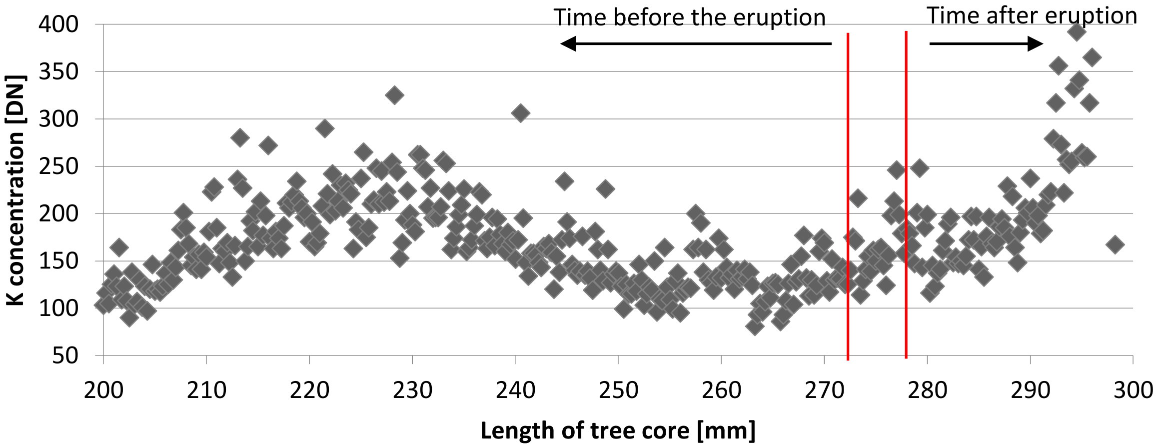


Figure 23: Concentrations of K in a tree core from the magic group.
In red is marked the beginning (left line) and the end (right line) of the year 2003, in which the eruption occurred (modified after Seiler 2014).

4.8. A model to predict "magic" soils

As none of the above discussed factors yields a sufficient explanation for the enhanced growth, and in most cases there was not even a significant difference at all, it might help to use a combination of all measured variables. This could help to distinguish the magic and control group and to see if there are any general differences.

A model was developed based on the measured variables, which gives as a result if a sample originates from the magic or control group. Input variables were: BDD, pH, total P, organic P, available P, NO_3^-, NH_4^+ and K. To establish the model, the means of magic and control group were calculated for all variables and then the overall mean of the two group means was assessed. For every variable a term was created after the following scheme:

$$T_{k,l} = a * b * \frac{M - J_{k,l}}{M}$$

Where:
T = value of the term for a variable k in a sample l
a = 1 or -1
b = weighing factor
M = mean of the two group means (overall mean)
J = Measured value of a variable k in a sample l

A is always 1, if the group mean of the magic group is smaller than the overall mean (which is the case for pH, NO_3^- and K) and -1 if the magic mean is larger than the overall mean (which is the case for BDD, total, organic and available P, NH_4^+). The weighing factor is always 1 except for total P, available P and NO_3^-, where it is 0.2. Notice that the weighing factor was just empirically derived by calibrating the model.

For a specific sample, all individual terms for each variable are then summed up and yield a number. A negative number indicates, that the sample belongs to the control group, whereas a positive number indicates the belonging to the magic group. The larger the numbers, the larger is expressiveness of the classification.

An example, taken from sample P013:

Sample Number	**BDD**	**pH**	**P tot**	**P org**	**P av**	**NH4**	**NO3**	**K**
M P013	1.08	5.03	0.92	0.25	2.47	1.59	10.79	15.63
Mean Magic	0.97	4.98	0.77	0.12	2.57	3.56	22.75	17.79
Mean Control	0.92	5.10	0.72	0.07	2.13	3.14	24.44	21.22
Overall Mean	0.94	5.04	0.75	0.10	2.35	3.35	23.60	19.51

Table 10: Input data for the model (rounded).
(Units are not necessary, because they are always normalized to ratios, which are unitless).

The first term (BDD) is then calculated as follows:

$$-1 * 1 * \frac{0.94 - 1.08}{0.94} = 0.148$$

Adding up all terms results in:

$\sum_{k=1}^{7} T_{j,k}$ = 0.148 + 0.001 + 0.046 + 1.595 + 0.010 - 0.526 + 0.109 + 0.199 = **1.581**

The value is positive and therefore indicating the belonging of the sample to the magic group. Applied to all samples, the reliability of the model was 90%, meaning that 18 of 20 samples were classified correctly.

Unfortunately, it was not possible to sufficiently validate the model. It would be very interesting to have some more samples from the study area and to be able to test, whether this model holds true for more samples.

This model was designed to have a possibility to differentiate between the two groups and being able to classify a distinct sample into a group, based on its variables. However, the question of the origin of the differences is highly unclear. Most likely it only reflects the spatial distance and to some degree the empirical derivation of the model. More samples to validate the model would be the consequent continuation of the model purpose.

5. Conclusions

The results of the measurements and analyses of this study did not support the hypotheses. Although there were some minor differences between magic and control groups, the origin of these differences remains unclear and is in most cases unlikely to be produced by some process preceding the 2003 eruption. The difference between the stronger grown trees and the normally grown ones cannot be attributed to distinct soil properties, at least not measurable ten years later. Phosphorus, potassium, nitrate and ammonium play important roles in the nutrition and the growth of plants, but their supply did not seem to cause the difference. A change in pH and a corresponding change of nutrient availability might have happened, as pH was indeed significantly different. Accounting for the NDVI signal, it has to be assumed that the difference in pH was larger during the time before the eruption, as the measured differences were clearly too small to explain an enhanced vegetation activity.

However, carbon would be interesting to investigate more profoundly, as it was tested significant for the two groups and is one of the most important variables in soils. Furthermore, the total carbon is not expected to change very quickly throughout time. Organic phosphorus might as well be interesting to investigate further, because the differences between the two groups were actually quite high, but the number of samples was too low and the variance within the groups too big to result in an appropriate *p*-value when tested.

Though the hypotheses could not be held, this study gives an insight in many properties, factors and nutrients, characterizing and influencing a volcanogenic soil. Furthermore there were minor differences found, which were also supported by the model. So even if these differences cannot explain what happened before the eruption, they might still represent processes, which also had an impact on the soils and not only on the plants.

For future investigations and research on this topic, the measured values can already give a starting point and values for comparison in a system with high heterogeneity and variance. The experimental design has probably to be improved in some points, as the distance between magic samples was never as large as the distance between a magic and any control sample, making it very hard to proof the difference not originating from this spatial distance. Therefore, it is proposed to use trees which were close to the NDVI line, but did not show a signal in the tree rings as control group, leading to more meaningful causal relationships in the analyses.

Certainly there are problems concerning the timescale as well. Sampling a soil ten years after a special event does not necessarily show anything, even if there was once a difference. If the enhanced plant growth is supposed to be explained, then it is crucial to search for an enhanced NDVI like this in more and recent remote sensing datasets to sample trees and soil as quickly as possible after or even before the eruption.

Furthermore, some alternative explanations of the strange data have to be considered. Volcanic degassing or vertical heat transport are potential explanations for faster plant growth, yet it is extremely difficult to assess such changes, above all so long after it happened.

Acknowledgement

I would like to thank many people, who made this Thesis just possible.

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References

Literature

Acocella V, Neri M (2003) What makes flank eruptions? The 2001 Etna eruption and its possible triggering mechanisms. Bulletin of Volcanology 65:517-529

Aiuppa A, Moretti R, Federico C, Giudice G, Gurrieri S, Liuzzo M, Papale P, Shinohara H, Valenza M (2013) Forecasting Etna eruptions by real-time observation of volcanic gas composition. Geology 35(12):1115-1118

Alef K (1991) Methodenhandbuch der Bodenmikrobiologie. Ecomed, Landsberg/Lech

Anda M, Sarwani M (2012) Mineralogy, Chemical Composition, and Dissolution of Fresh Ash eruption: New Potential Source of Nutrients. Journal of the Soil Science Society of America 76:733-747

Arnalds O, Stahr K (2004) Volcanic soil resources: occurrence, development, and properties. Catena 56(1-3):1-2

Bates RG (1973) Determination of pH: Theory and Practice. Wiley, New York

Batjes NH (1996) Total carbon and nitrogen in the soils of the world. European Journal of Soil Science 47:151-163

Branca S, Coltelli M, DeBeni E, Wijbrans J (2007) Geological evolution of Mount Etna volcano (Italy) from earliest products until the first central volcanism (between 500 and 100 ka ago) inferred from geochemical and stratigraphic data. International Journal of Earth Sciences 97(1):135-152

Buckman HO, Brady NC (1960) The nature and properties of soils. The Macmillan Company, New York, p 567

Busman L, Lamb J, Randall G, Rehm G, Schmitt M (2009) The nature of phosphorus in soils. In: Regents of the University of Minnesota, Minnesota

Buurman P, Van Langen N, Velthorst EJ (1996) Manual for Soil and Water Analysis. Backhuys Publishers Leiden, Wageningen

Caliro S, Chiodini G, Avino R, Cardellini C, Frondini F (2005) Volcanic degassing at Somma-Vesuvio (Italy) inferred by chemical and isotopic signatures of groundwater. Applied Geochemistry 20:1060-1076

Dazzi C (2007) Environmental features and land use of Etna (Sicily - Italy). In: Arnalds O, Bartoli F, Buurman P, Oskarsson H, Stoops G, Garcia-Rodeja E (eds) Soils of Volcanic Regions in Europe. Springer-Verlag Berlin, Heidelberg

De Carolis C, Lo Giudice E, Tonelli AM (1976) The 1974 Etna Eruption: Multispectral Analysis of Skylab Images Reveals the Vegetation Canopy as likely Transducer of Pre-eruptiveVolcanic Emmisions. Bulletin of Volcanology 39(3):371-384

DelNegro C, Cappello A, Neri M, Bilotta G, Hérault A, Ganci G (2013) Lava flow hazards at Mount Etna: constraints imposed by eruptive history and numerical simulations. Scientific Reports 3

Dipartimento della Protezione Civile (1995) Pianificazione nazionale d'emergenza dell'area vesuviana. In: Dipartimento della Protezione Civile (ed), Italy

do Carmo Horta M, Torrent J (2007) The Olsen P method as an agronomic and environmental test for predicting phosphate release from acid soils. Nutrient Cycling in Agroecosystems 77:283-292

Egli M, Filip D, Mavris C, Fischer B, Götze J, Raimondi S, Seibert J (2012) Rapid transformation of inorganic to organic and plant available phosphorus in soils of a glacier forefield. Geoderma 189:215-226

Egli M, Mastrolonardo G, Seiler R, Raimondi S, Favilli F, Crimi V, Krebs R, Cherubini P, Certini G (2012) Charcoal and stable organic matter as indicators of fire frequency, climate and past vegetation in volcanic soils of Mt. Etna, Sicily. Catena 88:14-26

Ferrara V (1975) Idrogeologia del versante orientale dell'Etna. Chapman and Hall, London

Fierotti G, Dazzi C, Raimondi S (1988) Carta dei Suoli della Sicilia. Regione Siciliana Assessorato Territorio ed Ambiente. In: Università degli Studi di Palermo, Facoltà di Agraria, Istituto di Agronomia Generale, Cattedra di Pedologia, Palermo

Fischer RV, H.-U. S (1984) Pyroclastic rocks. Springer Verlag, Heidelberg

Giammanco S, Bonfati P (2009) Cluster analysis of soil CO2 data from Mt. Etna (Italy) reveals volcanic influences on temporal and spatial patterns of degassing. Bulletin of Volcanology 71(2):201-218

Giammanco S, Ottaviani M, Valenza M, Veschetti W, Principio E, Giammanco G, Pignato S (1998) Major and trace elements geochemistry in the ground waters of a volcanic area: Mount Etna (Sicily, Italy). Water Resources 32(1):19-30

Giese P (1987) Ozeane und Kontinente. Spektrum Akademischer Verlag, Heidelberg

Greenwood NN, Earnshaw A (1997) Chemistry of the Elements. Butterworth-Heinemann, Oxford

Haynes RJ (1986) Mineral nitrogen in the plant-soil system. Academic Press, Orlando

Houlie N, Briole P, Bonforte A, Puglisi G (2006) Large scale ground deformation of Etna observed by GPS between 1994 and 2001. Geophysical Research Letters 33

Houlie N, Komorowski JC, de Michele M, Kasereka M, Ciraba H (2006) Early detection of eruptive dykes revealed by normalized difference vegetation index (NDVI) on Mt. Etna and Mt. Nyiragongo. Earth and Planetary Science Letters 246:231-240

Jenny H (1941) Factors of Soil Formation: A System of quantitative pedology. McGraw-Hill, New York

Keller J (2004) Vulkanismus: Gefahren und Vorhersage. In: Thiede JE, Lothar; Emmermann, Dietrich, Herm; Seibold, Eugen; Spielhagen, Robert, F.; Wedepohl, Karl, Hans; Winiger, Matthias (ed) Geowissenschaften und die Zukunft. Franz Steiner Verlag, Stuttgard

Kilburn CRJ (2003) Multiscale fracturing as key to forecasting volcanic eruptions. Journal of Volcanology and Geothermal Research 125:271-289

Kuo S (1996) Phosphorus. In: Sparks DL (ed) Methods of Soil Analysis, Part 3 - Chemical Methods (SSSA Book Series 5). Soil Science of America, Madison, pp 869-919

Lakanen E, Erviö R (1971) A comparison of eight extractants for the determination of plant-available micronutrients. Acta Agralia Fennica 123:223-235

Manning SW, Ramsey CB, Kutschera W, Higham T, Kromber B, Steier P, Wild EM (2006) Chronology for the Aegean Late Bronze Age 1700 - 1400 B.C. Science 312:565-569

Marzocchi W, Sandri L, Gasparini P, Newhall C, Boschi E (2004) Quantifying probabilities of volcanic events: the example of volcanic hazard at Mount Vesuvius. Journal of Geophysical Research 109

Meason DF, Idol TW, Friday JB, Scowcroft PG (2009) Effects of fertilisation on phosphorus pools in the volcanic soil of a managed tropical forest. Forest Ecology and Management 258:2199-2206

Mengel K (1961) Ernährung und Stoffwechsel der Pflanze. Fischer, Jena

Pearson K (1901) On lines and Planes of Closest Fit to Systems of Points in Space. Philosophical Magazine 2(11):559-572

Pichler H (1984) Italienische Vulkan-Gebiete IV: Ätna, Sizilien. Gebrüder Borntraeger Berlin, Stuttgart

Press F, Siever R (2003) Allgemeine Geologie. Einführung in das System Erde. Spektrum, Berlin, p 723

Rast H (1983) Vulkane und Vulkanismus. Ferdinand Enke Verlag, Stuttgard

Rolandi G (2010) Volcanic hazard at Vesuvius: An analysis for the revision of the current emergency plan. Journal of Volcanology and Geothermal Research 189:347-362

Schmincke H-U (2000) Vulkanismus. Wissenschaftliche Buchgesellschaft, Darmstadt

Sinkin T, Siebert L (1984) Explosive eruptions in space and time: durations, intervals, and comparison of the world's active volcanic belts. In: Explosive volcanism: inception, evolution, and hazards. Net Acadamy Press, Washington, pp 110-121

Solana MC, Kilburn CRJ, Rolandi G (2008) Communicating eruption and hazard forecasts on Vesuvius, Southern Italy. Journal of Volcanology and Geothermal Research 172:308-314

Sonzogni E (2011) Alberi e Vulcani: Effetti dell'eruzione (1950-51) del vulcano Etna sull'accrescimento degli alberi. In: Department of Geography. University of Zurich, Zurich

Sørensen SPL (1909) Enzymstudien II: Mitteilung. Über die Messung und die Bedeutung der Wasserstoffionenkoncentration bei enzymatischen Prozessen. Biochemische Zeitschrift 21:131-304

Stahr K, Kandeler E, Herrman L, Streck T (2012) Bodenkunde und Standortlehre, Grundwissen Bachelor. Eugen Ulmer, Stuttgard

Tanguy JC, Condomines M, Kieffer G (1997) Evolution of the Mount Etna magma: constraints on the present feeding system and eruptive mechanisms. Journal of Volcanology and Geothermal Research 75:221-250

Tilling RI, Lipman PW (1993) Lessons in reducing volcano risk. Nature 364:277-280

Winogradsky S (1892) Recherches sur les organismes de la nitrification. In: Annales de l'Institut Pasteur. Paris, pp 213-231; 257-275; 760-771

WRB IWG (2006) World reference base for soil resources 2006. In: World Soil Resources Reports. FAO, Rome

Figures

Title page: Ruedi Seiler.

Figure 1: Messer, Woland (2006): http://upload.wikimedia.org/wikipedia/commons/9/97/Volcano_scheme.svg (accessed: 28.4.2014).

Figure 2: Houlie, N., J. C. Komorowski, M. de Michele, M. Kasereka & H. Ciraba (2006b) Early detection of eruptive dykes revealed by normalized difference vegetation index (NDVI) on Mt. Etna and Mt. Nyiragongo. Earth and Planetary Science Letters, 246, 231-240.

Figure 3: DelNegro, C., A. Cappello, M. Neri, G. Bilotta, A. Hérault & G. Ganci (2013) Lava flow hazards at Mount Etna: constraints imposed by eruptive history and numerical simulations. Scientific Reports, 3.

Figure 4: Mühr, Bernhard (2002): http://www.klimadiagramme.de/Europa/catania.html (accessed 28.4.2014)

Figure 5: Ruedi Seiler

Figure 6: self-made

Figure 7: personal photograph

Figure 8: personal photograph

Figure 9: self-made

Figure 10: self-made

Figure 11: self-made

Figure 12: self-made

Figure 13: self-made

Figure 14: self-made

Figure 15: self-made

Figure 16: self-made

Figure 17: self-made

Figure 18: self-made

Figure 19: self-made

Figure 20: self-made

Figure 21: Dréo, Johann (2009): http://upload.wikimedia.org/wikipedia/commons/f/fe/Nitrogen_Cycle.svg (accessed, 5.5.2014)

Figure 22: Ruedi Seiler (unpublished).

Figure 23: Ruedi Seiler (unpublished)

Appendix A

These are the notes for every soil profile, where the samples were taken. Completeness of the given data cannot be guaranteed.

Magic

N002

Coordinates: N37°48.323’ E15°02.404’

Elevation: 1839 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 4-5 cm; 10R 2/1 (dry).

L horizon in the A horizon: 2-3 cm; 5YR 2/2 (wet).

B horizon: > 25 cm; 5YR 2/1 (dry).

Exposition: flat.

Comments: Distance to tree was 1 m, situated directly next to the lava flow.

N027

Coordinates: N37°48.308’ E15°02.368’

Elevation: 1841 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 3 cm; spotted 10YR 2/1 and 10YR ¾.

B horizon: > 30 cm; 10YR 4/3.

Exposition: Declination: 310°; Inclination: 10°.

Comments: Distance to tree was 1 m.

P013

Coordinates: N37°48.361’ E15°02.357’

Elevation: 1852 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 7 cm; 5YR 1.7/1.

L horizon in the A horizon: 2-3 cm; bright brown.

B horizon: > 25 cm; 7.5YR 3/2.

Exposition: flat.

Comments: Distance to tree was 1 m.

N022

Coordinates: N37°48.340’ E15°02.441’

Elevation: 1837 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 1-2 cm.

B horizon: > 30 cm; 10YR 2/2.

Exposition: flat.

Comments: Distance to tree was 2 m. Very high amount of sand. 10 m from lavaflow.

S006

Coordinates: N37°48.341’ E15°02.504’

Elevation: 1826 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 2 cm; 10R 1.7/1.

L horizon in the A horizon: 1 cm.

Upper B horizon: 10 cm; 7.5YR 1.7/1.

C horizon: from 12 cm.

Lower B horizon: > 15 cm; 10YR 4/4.

Exposition: Declination: 315°; Inclination: 10°.

Comments: Distance to tree was 2 m. 5 m to the lava flow.

P007

Coordinates: N37°48.247’ E15°02.397’

Elevation: 1851 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 20 cm; 7.5YR 3/2.

C horizon: 1 cm; only gravel (grey).

B horizon: > 15 cm; 10YR 3/3.

Exposition: flat.

Comments: Distance to tree was 4 m. 7 m from lava flow.

P002

Coordinates: N37°48.185’ E15°02.415’

Elevation: 1841 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 12 cm; 7.5YR 2/2.

L horizon in the A horizon: 1 cm.

B horizon: >25 cm; 10YR 3/2.

Exposition: flat.

Comments: Distance to tree was 2 m. 50 m to the lava flow.

N016

Coordinates: N37°48.273’ E15°02.505’

Elevation: 1834 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 5 cm; 10YR 1.7/1.

Upper B horizon: 20 cm; 7.5YR 3/3.

C horizon: 5 cm; black.

Lower B horizon: > 15 cm; 10YR 3/4.

Exposition: flat.

Comments: Distance to tree was 4 m. On island between two lava flows.

N017

Coordinates: N37°48.263’ E15°02.533’

Elevation: 1825 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 3 cm; 10YR 1.7/1.

Upper B horizon: 25 cm; 10YR 2/3.

C horizon: from 30 cm on. Gravel.

Exposition: flat.

Comments: Distance to tree was 1.5 m. On island between lava flows.

N013

Coordinates: N37°48.275’ E15°02.532’

Elevation: 1832 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 2 cm; 10R 1/1.

Upper B horizon: 6 cm; 10YR 2/2.

C horizon: 8 cm.

Lower B horizon: > 20 cm; n.a.

Exposition: flat.

Comments: Distance to tree was 2 m. 2 m to the lava flow.

Control

C06/07_1:

Coordinates: N37°47.275’ E15°03.723’

Elevation: 1631 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 4 cm; 7.5YR 1.7/1.

L in A horizon: 2 cm; 7.5YR 3/2.

Upper B horizon: 13 cm; 7.5YR 4/2.

C horizon: 4 cm; 7.5YR 2/2.

Lower B horizon: > 20 cm; 10YR 4/3.

Exposition: Declination: 55°; Inclination: 19°.

Comments: Distance to tree was 1 m.

C06/07_2:

Elevation: 1630m a.s.l.

Thickness/Munsell Colour: Same as C06/07_1.

Exposition: flat.

Comments: 4 m away from C06/07_1, below the slope.

C06/07_3:

Elevation: 1633m a.s.l.

Thickness/Munsell Colour: Same as C06/07_1.

Exposition: flat.

Comments: 10 m away from C06/07_1, above slope.

C08/09_1:

Coordinates: N37°47.392’ E15°03.665’

Elevation: 1622 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 7 cm; 2.5YR 3/1.

Upper B horizon: 6 cm; 7.5YR 2/2.

C horizon: 8 cm; 7.5YR 2/2.

Lower B horizon: > 15 cm; 5YR 4/4.

Exposition: Declination: 44°; Inclination: 18°.

Comments: Distance to tree was 10 m.

C08/09_2:

Elevation: 1624m a.s.l.

Thickness/Munsell Colour: Same as C06/07_1.

Exposition: flat.

Comments: 10 m away from C08/09_1, above the slope.

C01/02_1:

Coordinates: N37°48.095’ E15°03.018’

Elevation: 1647 m a.s.l.

Thickness/Munsell Colour of Soil Horizons:

A horizon: 2 cm; 7.5YR 1.7/1.

L below A horizon: 2 cm; 7.5YR 3/2.

Upper B horizon: 11 cm; 10YR 4/3.

C horizon: 7 cm; 10YR 4/3.

Lower B horizon: > 20 cm; 2.5Y 4/3.

Exposition: flat.

Comments: Distance to tree was 2 m.

C01/02_2:

Elevation: 1650m a.s.l.

Thickness/Munsell Colour: Same as C06/07_1.

Exposition: Declination: 30°; Inclination: 25°

Comments: 20 m away from C01/02_1.

C01/02_3:

Coordinates: N37°48.085’ E15°03.004’

Elevation: 1652m a.s.l.

Thickness/Munsell Colour: Same as C01/02_1 and C01/02_2.

Exposition: flat.

Comments: 10 m upwards from C01/02_2.

C01/02_4:

Coordinates: N37°48.212’ E15°03.103’

Elevation: 1670m a.s.l.

Thickness/Munsell Colour: Similar to C01/02_1 and C01/02_2.

Exposition: Declination: 19°; Inclination: 22°.

Comments: 30 m upwards from C01/02_3.

C01/02_5:

Elevation: 1670m a.s.l.

Thickness/Munsell Colour: Same as C01/02_4

Exposition: flat; in a depression.

Comments: right next to C01/01_4.

Appendix B

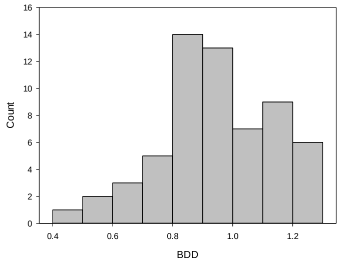
Statistical Analyses of the soil properties

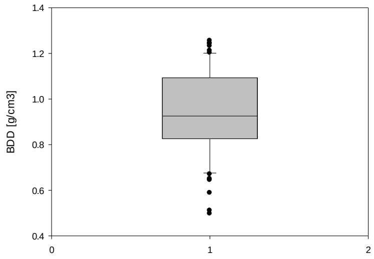
1. Bulk Dry Density

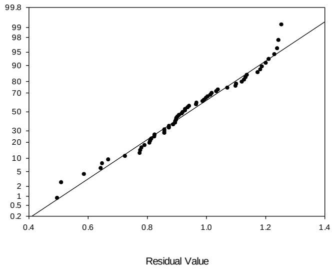
Descriptive Statistics for BDD:

Group	Mean	Depth	Mean
magic	0.967	0-10cm	0.884
control	0.915	10-20cm	0.974
		20-30cm	0.965

BDD passes a Shapiro-Wilkinson-Test with a P-Value of 0.207.
BDD passes equal variance with a P-Value of 0.076.







As one can see in the Histogram, Boxplot and P-P-Plot the data is definitely not well normally distributed. However, as the differences are not significant we can assume that if we had a large enough dataset, the data would indeed be normally distributed.
An ANOVA was carried out with the function (used for all ANOVAS here):

data = f(group x depth)
where: group = magic or control
depth = 0-10cm; 10-20cm; 20-30cm

ANOVA results are:

Source of Variation	DF	SS	MS	F	P
Group	1	0.0411	0.0411	1.227	0.273
Depth	2	0.0976	0.0488	1.459	0.242
Group x Depth	2	0.0116	0.00580	0.173	0.841
Residual	54	1.808	0.0335		
Total	59	1.958	0.0332		

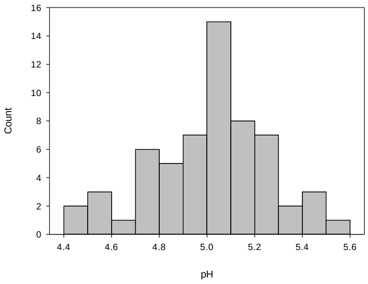
The ANOVA shows no P-Value below 0.05 and therefore we have no significant difference between groups or depth for the BDD.

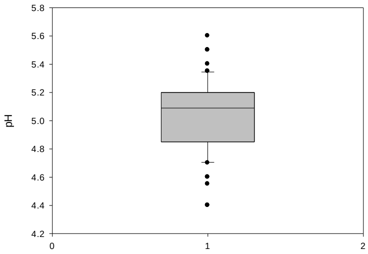
2. pH

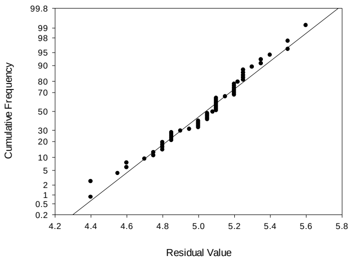
Descriptive Statistics for pH:

Group	Mean	Depth	Mean
magic	4.978	0-10cm	4.899
control	5.098	10-20cm	5.028
		20-30cm	5.188

pH passes a Shapiro-Wilkinson-Test with a P-Value of 0.172.
pH passes equal variance with a P-Value of 0.386.







Histogram and P-P-Plot show slightly too high values near the mean of the dataset, resulting from a Kurtosis of 0.297. However, the dataset does not seem to be far from normal distribution, making it possible to use an ANOVA.
Results are:

Source of Variation	DF	SS	MS	F	P
Group	1	0.216	0.216	4.289	0.043
Depth	2	0.835	0.418	8.293	<0.001
Group x Depth	2	0.0112	0.00560	0.111	0.895
Residual	54	2.719	0.0504		
Total	59	3.782	0.0641		

Here the result suggests on one hand a strongly significant difference in pH with depth, which is very much logic in a soil. On the other hand the difference from magic and control is also significantly different. However, when we compare the means of magic and control, which are 4.978 and 5.098, respectively, the difference is so small that although it is clearly detectable, the impact of this difference is assumed to be minimal in reality.

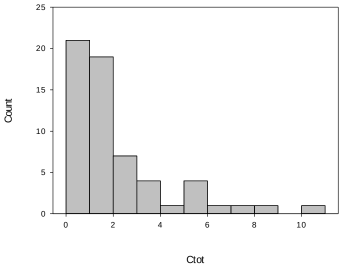
3. CHN

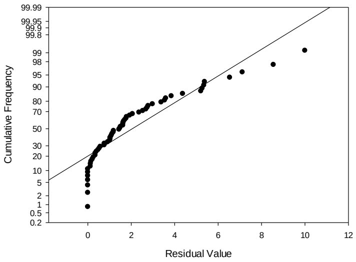
3.1 Total Carbon [%]

Descriptive Statistics for Ctot:

Group	Mean	Depth	Mean
magic	1.807	0-10cm	3.566
control	2.298	10-20cm	1.134
		20-30cm	1.456

Ctot clearly fails a Shapiro-Wilkinson-Test with a P-Value <0.001





It can also be easily seen in the Histogram and the P-P-Plot, that the distribution differs strongly from normal. Therefore a simple log-Transformation was carried out after the formula:

$data_{transformed} = \log(data + 1)$

Unfortunately the Shapiro-Wilkinson-Test still fails after log-Transformation with P: 0.037. Therefore a non parametric Man-Whitney U Rank Sum Test was carried out. Results are:

Group	N	Missing	Median	25%	75%
1.000	30	0	0.973	0.0900	2.705
2.000	30	0	1.640	1.025	3.420

Man-Whitney U Statistic= 315.500

T = 780.500 n(small)= 30 n(big)= 30 (P = 0.047)

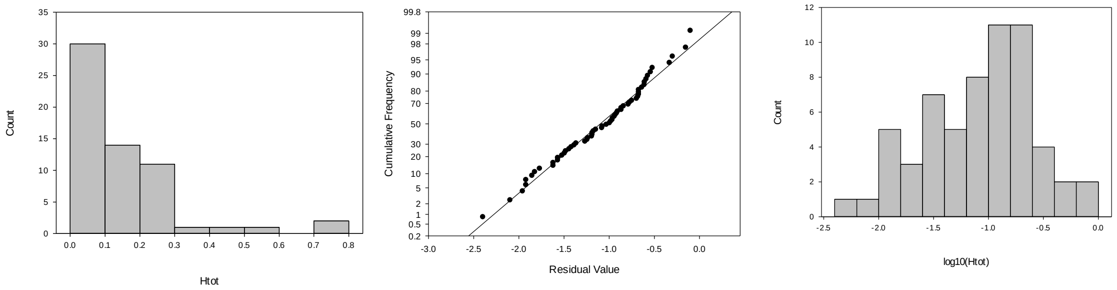
The P-Value suggests a significant difference in the two groups. This (regarding the group means from above) shows that in the control group is significantly more carbon, than in the magic group. Although these findings show indeed some differences between magic and control, one would rather expect the soils from the magic trees to have more carbon. Also the sampling methodology might have produced artefacts, if litter contaminated the samples from 0-10cm. A profound interpretation of these results certainly belongs into the discussion part of the Thesis.

3.2 Total Hydrogen [%]

Decriptive Statistics for Htot:

Group	**Mean**	**Depth**	**Mean**
magic	0.135	0-10cm	0.234
control	0.144	10-20cm	0.079
		20-30cm	0.106

Htot clearly fails a Shapiro-Wilkinson-Test with a P-Value <0.001



Histogram of Htot. Left: original; middle: after log-Transformation; right: P-P-Plot after log-Transformation. After the transformation a Shapiro-Wilkinson-Test was carried out and gave a P-Value of 0.216. With this normal distribution can be assumed.
Equal Variance passed with P-Value = 0.558.

Results of ANOVA:

Source of Variation	**DF**	**SS**	**MS**	**F**	**P**
Depth	2	2.555	1.278	5.999	0.004
Group	1	0.448	0.448	2.105	0.153
Depth x Group	2	0.318	0.159	0.748	0.478
Residual	54	11.500	0.213		
Total	59	14.822	0.251		

Depth is clearly significant, which can also be seen in the depth means, whereas the difference in group is not big enough to be detected by this test.

3.3 Total Nitrogen

Due to very low levels of Nitrogen, which were not detectable by the machine in Wädenswil, this data makes no sense to be analysed. Nitrogen is rather investigated indirectly via Ammonium and Nitrate (next page).

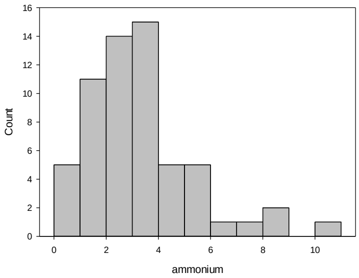
4. Ammonium and Nitrate

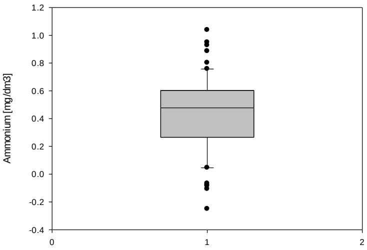
4.1 Ammonium

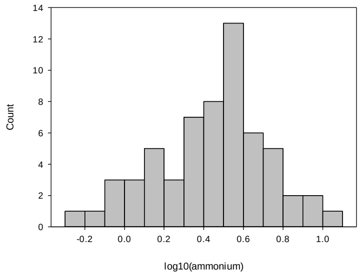
Descriptive statistics for NH4:

Group	Mean	Depth	Mean
magic	0.3563	0-10cm	0.4529
control	0.3142	10-20cm	0.2755
		20-30cm	0.2774

Shapiro-Wilkinson-Test clearly failed with a P-Value of < 0.001.
Due to its positive skewness (see left histogram), the data was log-transformed.







After transformation the data now passed the Normality-Test with a P-Value of 0.428, which is quite high, compared to most of the other datasets. Nevertheless, the histogram raises doubts about this normality, but again one can argue that if only large enough, the dataset would be normally distributed. The ANOVA gave the following results:

Source of Variation	DF	SS	MS	F	P
group	1	0.0289	0.0289	0.403	0.528
depth	2	0.651	0.325	4.532	0.015
group x depth	2	0.0525	0.0262	0.366	0.695
Residual	54	3.876	0.0718		
Total	59	4.608	0.0781		

Unfortunately equal variance test failed, so the ANOVA is not totally legitimate for this kind of test (Although the P-Value for the group is so high, that it seems very much unlikely to find a significant difference in any other test).

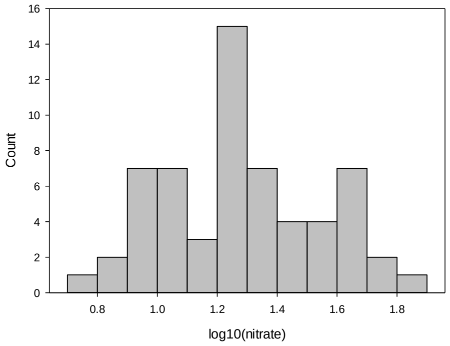
Concerning the variance, a simple Man-Whitney-U rank sum test was done with the initial dataset. The P-Value for this was even higher with 0.842, making it extremely unlikely to find a significant difference for the groups with the given methods and data.

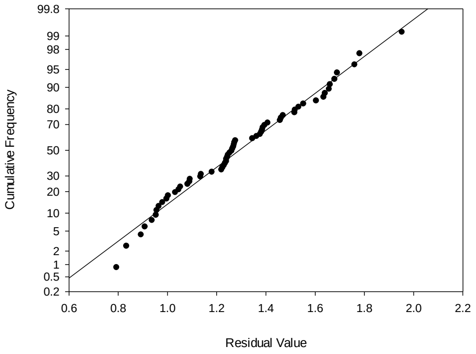
4.2 Nitrate

Descriptive statistics for NO3:

Group	**Mean**	**Depth**	**Mean**
magic	2.2754	0-10cm	3.5949
control	2.4443	10-20cm	1.8197
		20-30cm	1.6649

Shapiro-Wilkinson-Test failed with P-Value of < 0.001
The high skewness value of 1.787 favours again a log-transformation.





Histogram and P-P-Plot after transformation. And although it passed the Shapiro-Wilkinson-Test with P = 0.441 seems obvious that the data is still not normally distributed. Also the variance was tested to be different between the groups. Therefore a non parametric test had to be carried out. This was done with the initial dataset.

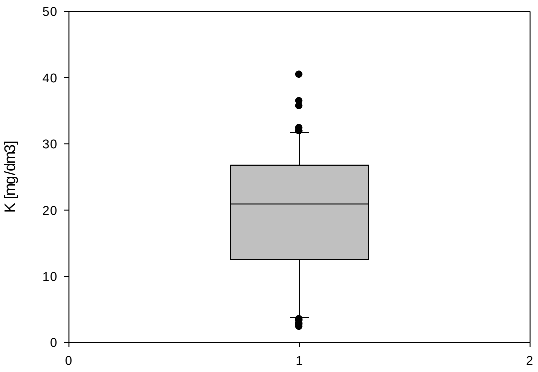
Man-Whitney-U rank sum test results: P-Value = 0.158 meaning that the difference is not big enough to be detected with this test. However the P-Value is quite low and it might be possible to detect a difference with a higher number of samples.

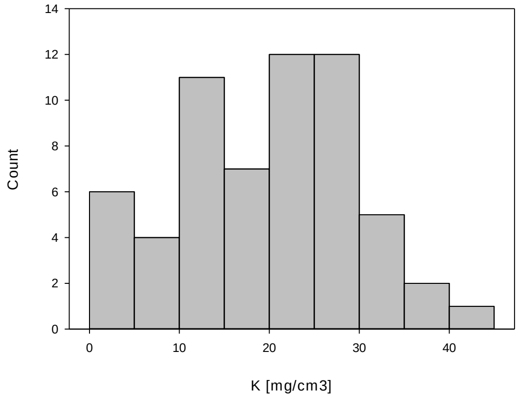
5. Plant available Potassium

Decriptive statistics for K:

Group	Mean	Depth	Mean
magic	17.786	0-10cm	25.542
control	21.224	10-20cm	15.091
		20-30cm	17.883

Normality test passed with a P-Value of 0.222
Equal Variance test passed with a P-Value of 0.780





Boxplot supports the assumption of normality whereas the histogram does not ultimately speak for normality. However with the tests passed and the assumption, that a large enough dataset would fulfil the criteria of normality one can use an ANOVA. Results are:

Source of Variation	DF	SS	MS	F	P
Group	1	177.316	177.316	2.472	0.122
Depth	2	1171.098	585.549	8.164	<0.001
Group x Depth	2	89.586	44.793	0.625	0.539
Residual	54	3873.121	71.724		
Total	59	5311.120	90.019		

Depth is one more time very strongly significant which is logic. Though the P-Value for the groups is too big for a significant difference it might be possible that there is indeed a significant difference which is only detectable with more samples. However, the mean values for group magic and control show that in any case the concentration of available Potassium would be higher in the control than in the magic, which counters the assumption of more fertile soils in the magic group.

6. Phosphorus

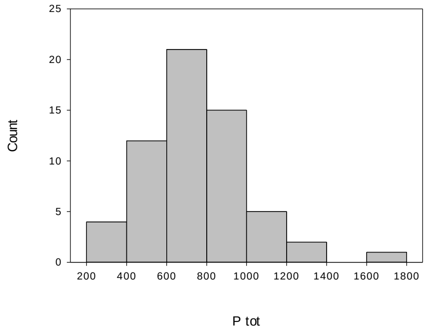
6.1 Total Phosphorus

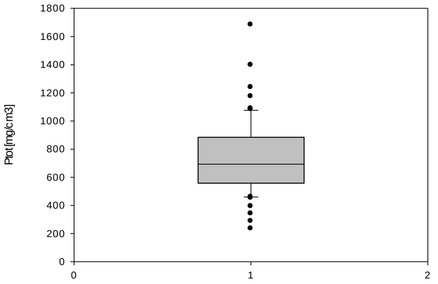
Descriptive Statistics for Ptot

Group	**Mean**	**Depth**	**Mean**
magic	0.774	0-10cm	0.676
control	0.722	10-20cm	0.743
		20-30cm	0.825

Shapiro-Wilkinson-Test passed with a P-Value of 0.054.
Equal Variance test passed with a P-Value of 0.668.

Although Shapiro-Wilkinson-Test is extremely close to finding a significant difference to normality, graphical representations support normality more clearly (histogram and boxplot below).





Although there is a slight positive skewness it looks rather normally distributed when we consider the two or three very high values as outliers. ANOVA yielded the following results:

Source of Variation	**DF**	**SS**	**MS**	**F**	**P**
group	1	39824.556	39824.556	0.595	0.444
depth	2	222318.310	111159.155	1.662	0.199
group x depth	2	37028.532	18514.266	0.277	0.759
Residual	54	3612512.617	66898.382		
Total	59	3911684.015	66299.729		

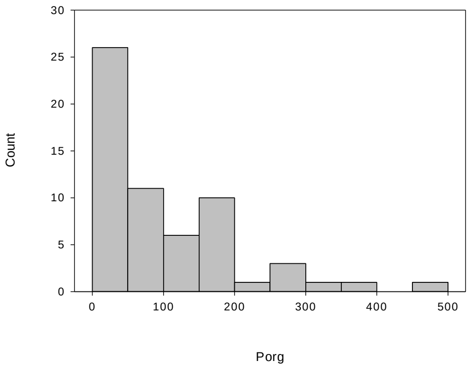
The P-Values indicate clearly that there is no detectable difference with the given methods.

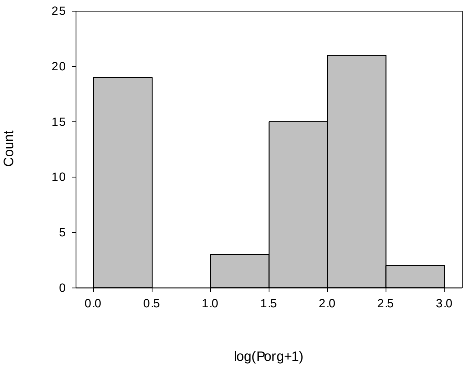
6.2 Organic Phosphorus

Descriptive Statistics for Porg:

Group	**Mean**	**Depth**	**Mean**
magic	0.122	0-10cm	0.080
control	0.070	10-20cm	0.112
		20-30cm	0.096

Normality clearly fails with Shapiro-Wilkinson-Test with a P-Value of < 0.001.





As it can be seen here the transformation does not really improve the extreme positive skewness in the original data. The problem is that many zero values prevent the dataset to be normally distributed. In this case once more a Man-Whitney-U test had to be carried out on the untransformed dataset.

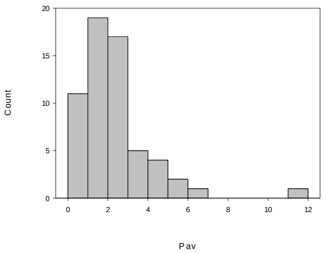
Results of the non parametric tests are: A P-Value of 0.139, indicating a small difference, yet too small to be significant. More samples might increase the possibility of getting a significant result.

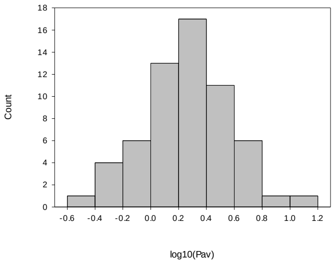
6.3 Plant Available Phosphorus

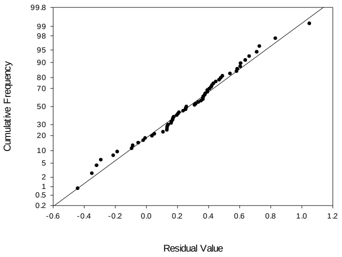
Descriptive Statistics for Pav:

Group	**Mean**	**Depth**	**Mean**
magic	2.567	0-10cm	3.392
control	2.134	10-20cm	2.230
		20-30cm	1.429

Shapiro-Wilkinson-Test clearly fails with P-Value < 0.001.
This can also be seen very nicely in the histogram on the left side. Due to its strong positive skewness a log-transformation was done. This resulted in very well normally distributed data, showed in the histogram in the middle and the P-P-Plot on the right side.







Equal Variance was tested after transformation and has passed with a P-Value of 0.891.
With this transformed dataset an ANOVA was carried out. With the following results:

Source of Variation	**DF**	**SS**	**MS**	**F**	**P**
group	1	0.00520	0.00520	0.0747	0.786
depth	2	1.330	0.665	9.553	<0.001
group x depth	2	0.150	0.0751	1.078	0.347
Residual	54	3.760	0.0696		
Total	59	5.246	0.0889		

Once more the depth is very significantly different which does still not surprise. Group did not show any sign of a significant difference in the concentration of available Phosphorus.

7. General Considerations to the Statistic Evaluation

-A lot of the soil properties datasets were not normally distributed although one normally would expect this in nature. This resulted partially from the experimental design, in which samples from different depth were taken. In the statistical analysis this caused sometimes trouble because in the upper layers there were mostly very different conditions than in the deeper layers, resulting in different values and often also different variances.
It is also possible that litter contaminated some 0-10cm samples, which could explain rare very high values in most datasets.

-When analysing the soils it is mostly logical to find strong differences between different layers/depths. This is because of the stratified nature of soils and the gradients in many organic and water soluble compounds from high in the surface to low in deeper layers, as the general input of such substances is usually onto the surface of the soil.

-The decision of either taking a parametric or a non-parametric test was not always easy, as it was mostly not 100% certain if the data could be assumed normally distributed or not.

Personal Declaration

I hereby declare that the submitted thesis is the result of my own, independent work. All external sources are explicitly acknowledged in the thesis.

Zürich, 25.6.2014

Moritz Reisser