Master Thesis

Influence of soil redox potential to emission of volatile organic compounds

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Abstract

The aim of the work was to establish a connection between the emission of volatile organic compounds (VOCs) from soil samples from the Schlöppnerbrunnen fen and the redox potential. For this purpose, two main experiments were carried out, which dealt with the anoxic incubation of the soil samples. First, the effect of drying out the soil samples over a period of two weeks under continuous N_2 gas flow was investigated. The second experiment dealt with the incubation of flooded soil samples in sealed glass bottles. In both cases a direct correlation between the increase of different VOCs and the redox potential could be established and therefore the main hypothesis could be confirmed.

Zusammenfassung

Das Ziel der Arbeit bestand darin einen Zusammenhang zwischen der Emission von flüchtigen organischen Stoffen (VOCs) aus Bodenproben des Schlöppnerbrunnen Moors und dem Redoxpotential herzustellen. Zu diesem Zweck wurden zwei Hauptexperimente durchgeführt, welche sich mit der anoxischen Inkubation der Bodenproben beschäftigten. Dabei wurde zunächst die Auswirkung der Austrocknung der Bodenproben über einen Zeitraum von zwei Wochen unter kontinuierlichem N_2 Gasfluss untersucht. Das zweite Experiment beschäftigte sich mit der Inkubation gefluteter Bodenproben in luftdicht verschlossenen Glasflaschen. In beiden Fällen konnte ein direkter Zusammenhang zwischen dem Anstieg verschiedener VOCs und dem Redoxpotential hergestellt und damit die Haupthypothese bestätigt werden.

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List of abbreviations

a (ox)	Activity of the oxidised form of the substance	[mol/l]
a (red)	Activity of the reduced form of the substance	[mol/l]
BVOCs	Biogenic volatile organic compounds	
c	Concentration	[mol/l]
CAS	Chemical Abstracts Service	
CI	Confidence interval	
cps	Counts per second	
d	Thickness of the cuvette	[cm]
dest.	Destilled	
DMS	Dimethyl sulfide	
DMSO	Dimethylsulfoxide	
DOM	Dissolved organic matter	
E_0	Standard redox potential	
ΔE^0	Change of the Redox potential	
E_N	Redox potential	
E_λ	Extinction	
ε_λ	Molar extinction coefficient at wavelength λ	[l/(mol*cm)]
F	Faraday constant	96.5 [kJ/(V*mol)]
ΔG^0	Gibbs energy	
GC	Gas chromatography	
GC-MS	Gas chromatography mass spectrometry	
GCU	Gas control unit	
I	Intensity of the transmitted light	
I_0	Intensity of exposure	
IR	Infra-red	
lg	Logarithm to base ten	
ln	Natural logarithm	
MFC	Mass flow controller	
MPI	Max-Planck-Institute	
MSA	Methane sulfonic acid	
P	Pressure	[Pa]
PE	Polyethylene	

pH	Pondus Hydrogenii (Hydrogen concentration)	
PHB	Poly-/L hydroxybutyric acid	
R	Universal gas constant	8.314 [J/(mol*K)]
SB II	Schlöppnerbrunnen II	
SIFT-MS	Selected Ion Flow Tube Mass Spectrometry	
SOM	Soil organic matter	
T	Temperature	[K]
V_m	Molar volume	[l/mol]
VOCs	Volatile organic compounds	
WEOM	Water-extractable organic matter	
WHC	Water holding capacity	
χ	Mixing ratio	[ppb]
z	Charge	
Φ	Flux of the substance	[mol/h]
ϕ	Gas flow	[l/h]

1 Introduction

The protection of our environment and habitat are central topics of today's time. But in order to protect it, it is necessary to understand the complex ecological relationships that have a huge impact on people's lives and health. Small volatile molecules can serve both as actors and indicators of chemical processes in certain habitats. For example, the behaviour of microorganisms and their influence on the Earth's various biochemical cycles plays an important role. An example of the far-reaching influence of volatile organic compounds (VOCs) is dimethyl sulfide (DMS), which is formed in soil by microorganisms, gets released and is converted into H_2SO_4 (over SO_2). This leads to acid rain, which is harmful for plants and waters.[1] Therefore, soil microbes are having huge impact on water- and air quality and on the possibilities of soil to produce food and building materials for world's population. Especially their participation in biogeochemical cycles of carbon, nitrogen, phosphorus and sulphur is essential. Furthermore, these emissions of VOCs allow conclusions about the metabolic processes in soils, which is an important source of information and enables a deeper understanding of the ecosystem and its dynamics. Hence, it's important to understand these mechanisms and to explore the impact of different factors on these cycles and their equilibrium.

1.1 Volatile organic compounds in soil

Biogenic volatile organic compounds (BVOCs) in soil are produced through microbial decomposition of plant residues or soil organic carbon,[2,3,4] root emission, evaporation of litter stored BVOCs,[5] and other physical processes.[6,7] They are released to the atmosphere but can also be absorbed by soils through biotic and abiotic uptake.[8,9] Like plant BVOCs, soil related BVOC emissions contribute to ecosystem emissions (10 %) and therefore impact atmospheric chemistry.[10,11] BVOCs are produced for signalling, communication, defence, and stimulation or inhibition of plant or microbial growth like aboveground plant volatile emissions.[12] The contribution of soil emissions to the total ecosystem fluxes of BVOCs are estimated to be between less than one percent[13] and tens of percent.[14] These estimations vary strongly between ecosystems, litter types and season and can contribute up to 20 % of the ecosystem emissions in the Arctic where no much plant biomass is available.[10]

Soils emit BVOCs because of microbial decomposition of soil organic matter (SOM) and plant residues, evaporation of stored compounds in leaf litter, and release of plant

metabolized BVOCs from roots. Because of their larger fraction of labile carbon and the release of stored BVOCs, leave litter generally emits higher rates of BVOCs than SOM.[4,15,16] Therefore, it has been suggested litter as the main BVOC source in forests besides vegetation.[17,18]

The age and quality of the litter as well as different SOM fractions also influence the microbial degradation and thus the BVOC emissions. Since the degradation of fresh litter generates less energy than the already aged litter and the degradation of needles takes longer than that of leaves, these parameters can influence the dynamics of BVOC emissions. Therefore, the time in the year as well as the location of the sampling is of great importance and can have a large influence on the results of the BVOC measurements.[19,16]

BVOCs synthesised by plants are often difficult to distinguish from soil emissions as they contribute to the measured emissions through root emissions and substances from the leaves in the litter. BVOCs produced in the rhizosphere can also be used by soil organisms, for example, as a fast carbon source. Therefore, the extent to which the removal of roots contributes to realistic soil emission measurements should be considered.[20,21,21]

BVOCs produced from SOM can be synthesized through different pathways of microbial metabolism. It is harder to separate SOM alone from the BVOC fluxes from root emissions because removal of the roots will destroy the soil structure. The measurement of root BVOC production without destroying the rhizosphere is difficult. Therefore, the common strategy is to compare emissions from root free soils with those from intact soils.[22] Thus, this measurements include the side effects.[23] Plant roots in soil are associated with mycorrhizal fungi and microbes and are synthesizing and emitting different compounds in the rhizosphere. How far they are contributing to the total soil BVOC emissions is not fully understood. Some studies have shown increased BVOC emissions by roots,[23,24] while others reported reduced emissions[13] or no impact on soil emissions.[18]

Biotic processes like microbial decomposition, release from litter storage and root production are influenced by water content and nutrient and oxygen availability and can lead to BVOC release as well as its consumption through microbes.[3,9] For example,

lowering the water table depth of peat cores can reduce the monoterpene emission and aerobic conditions in the A0 soil layer can lead to higher ethylene emissions.[25,26]

Abiotic, physical and chemical processes also influence VOC emissions, since the gas exchange between soil and atmosphere depends on the physical conditions of diffusion. Substances that remain in the earth can dissolve in water, remain in the gas phase or adsorb to soil particles. The dissolution and adsorption are depending on gas concentrations in the soil and can be influenced by its change. Some studies have indicated that abiotic sources of VOCs are generally less important than biotic ones and may influence short term patterns in VOC fluxes.[27,4] Since abiotic factors such as diffusion processes depend on temperature, larger temperature differences can have an impact on BVOC emissions. Higher temperatures can also increase the activity of microorganisms and thus influence their BVOC production. Therefore, it is often difficult to distinguish temperature induced abiotic changes from biotic processes.[28]

Dimethyl sulphide (DMS) is an important soil BVOC. It has been detected in Litter and SOM emissions under laboratory and field conditions and can be released as well as absorbed by soil.[29,30] One possible source is the aerobic microbial metabolism of sulphur containing amino acids.[29]

Since sulphur metabolites such as DMS are often produced in soil by microbial activities and interact with different ecosystems, the understanding of their production and further reactions is a first step towards the investigation of soil chemical processes and their effects.

1.2 Volatile sulphur metabolites

Important volatile metabolites are DMS, sulphur dioxide (SO_2), carbon sulphide (COS) and methanethiol. They are part of the sulphur cycle whose basic processes are shown in Figure 1.[31] DMS is a volatile compound, which is a gas emitted from soil which works against the greenhouse effect. It gets oxidised in the Atmosphere to dimethyl sulfoxide (DMSO) and further to SO_2 and other products. This oxidation process can be caused by OH radicals. The hydroxide radicals are formed due to ultraviolet (UV) radiation in the atmosphere. Measurement data of other oxidation products like sulphur dioxide (SO_2), sulfuric acid (H_2SO_4), dimethyl sulfoxide (CH_3SOCH_3, DMSO), dimethyl sulfone ($CH_3SO_2CH_3$, $DMSO_2$), and methane sulfonic acid ($CH_3S(O)_2OH$, MSA) were found through field studies. Starting from SO_2 sulphate (SO_4^{2-}) can be formed which act

as condensation nuclei for water vapor. The clouds that form from these condensation nuclei can deflect more incoming radiation back into space and thereby reduce the temperature on earth.[32,33] But SO_4^{2-} can also cause acid rain which is harmful for plants and waters.[34]

Acid rain makes waters more acidic, which results in more aluminium absorption from soil, which is carried into lakes and streams. That combination makes waters toxic to crayfish, clams, fish, and other aquatic animals. Also, forests are damaged by acid rain and fog, especially those at higher elevations. The acids bind to essential nutrients in soil such as calcium, so they are no longer available for plants. They also cause aluminium to be released in soil, which makes it hard for trees to take up water. The leaves and needles of the plants also get harmed and they are less healthy and more vulnerable to cold temperatures, insects and disease.[35,36,1]

The starting substance of both of this reaction DMS is produced by soil bacteria. It can be synthesized by decomposition of organic material that contains sulphurous amino acids like methionine, methionine sulphone, methionine sulphoxide and S-methyl cysteine.[37] Another way of microbial DMS production is based on a methyltransferase enzyme, which catalyses the methylation of MeSH, which is used by a wide range of bacteria and some cyanobacteria.[38]

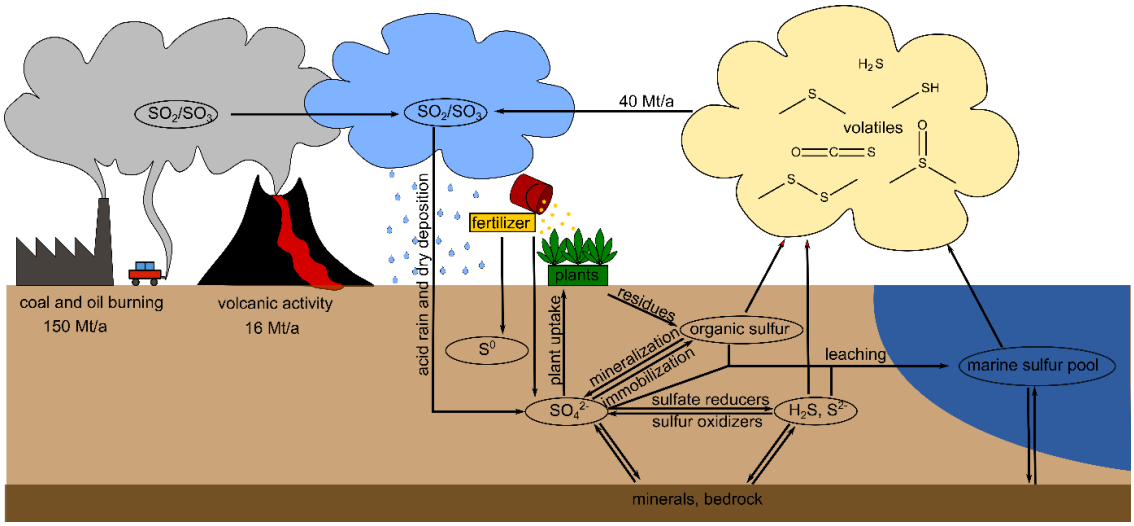

Figure 1: Visualization biogeochemical sulphur cycle between sediments, oceans, continents, the atmosphere and stratosphere (created by Ann-Sophie Lehnert, MPI Jena).

The knowledge about the different possibilities of VOC and especially volatile sulphur compound production allows the planning of tests and the selection of control samples. However, these must then be analysed in order to verify the hypotheses previously

made. For this purpose, there are various methods which can be used for analysis. Emissions from soil samples can be analysed by Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), Raman spectroscopy or IR spectroscopy. Each method has certain advantages and disadvantages. Therefore, the method should be selected according to hypothesis, sample size and research question.

1.3 Comparison of SIFT-MS, Raman- and IR-spectroscopy

There are several ways to measure VOC emissions from soils. Which method of analysis should be used depends on the requirements of the experiment, as each method has certain advantages and disadvantages.

One method for measuring VOCs is structure elucidation using IR spectrometry, which is based on the identification of functional groups using the IR absorption spectrum of the substance to be analysed. In addition, Lambert Beer's law can be used for quantification (cf. Equation 1).For the separation of a sample mixture, it is possible to combine IR spectroscopy with GC. An advantage of IR spectroscopy is that only a relatively small sample is required, and this is not changed by the analytical method. A low preparation effort as well as comparability of the experiments due to the established nature are further reasons for the use of IR spectroscopy. The disadvantage of this method is the effort required to evaluate the spectra and the duration of the GC separation and measurement, which is disadvantageous for larger sample quantities.[39,40,41]

Equation 1: Lambert Beer's law. E_λ: Extinction, I: Intensity of the transmitted light, I_0: Intensity of exposure, c: Concentration of the absorbing substance in the solution ($mol*l^{-1}$), ε_λ: Molar extinction coefficient at wavelength λ ($l*mol^{-1}*cm^{-1}$), d: Thickness of the cuvette (cm).

$$E_\lambda = -\lg\left(\frac{I}{I_0}\right) = \varepsilon_\lambda * c * d$$

Raman spectroscopy is another analytical method for gas emissions from soils. In contrast to absorption measurement in IR spectroscopy, Raman spectroscopy measures the scattering of light. This is generated by the change of the vibrational state of the particular molecule. Since the oscillation spectrum of each substance is different, it can be identified by its characteristic molecular fingerprint. In contrast to IR spectroscopy, quantification is linear to the intensity of the Raman bands in the spectrum.

An advantage of Raman spectroscopy is that no sample preparation is necessary and there is no interference from water. Furthermore, the samples are not altered, and the specificity is very high due to the chemical fingerprint. The method can also be per-

formed quickly. Disadvantages are that it cannot be used for metals or alloys. In addition, fluorescence or contamination of the sample can lead to incorrect results. The fact that the sample can heat up due to laser irradiation can destroy it or falsify the spectrum. However, one of the main disadvantages is the low sensitivity of the method due to the weak Raman effect.[42,43,44]

The method used to analyse the soil samples in this thesis is SIFT-MS. The molecules of the sample are ionized by precursor ions and then measured at the detector. In contrast to IR and Raman spectroscopy, no prior separation of the sample mixture is necessary. Furthermore, this method has a significantly higher sensitivity, which even allows the detection of traces. Another advantage is that operation is simple, and no special training is required. The real time measurement also allows the samples to be analysed over longer periods of time under different conditions, since no sample preparation is required. Thus, the analysis with SIFT-MS is best suited for the experiments described in this thesis.[45,46]

1.4 SIFT-MS

SIFT-MS is an analytical method for real time quantification of different gases. It is based on chemical ionisation of the gas molecules through H_3O^+, NO^+ and O_2^+ precursor ions and Helium is used as carrier gas.[47] The precursor Ions are formed by microwave discharge through moist or dry air. The reagent ion of choice is then selected using a quadrupole mass filter. This method is commonly used for breath analysis but can also be used for examination of volatile organic compounds (VOCs) in other gases. With the characteristic product ions, it is possible to determine the different gas components, and their intensity. The flow through the flow tube leads to a defined reaction time, which enables the subsequent quantification of the analyte. The basic composition of a SIFT-MS is shown in Figure 2. Thereby the gas encounters the carrier gas inside of the instrument. The ionisation source generates reaction ions which are ionising the molecules of the gas sample. Therefore, they can be separated after their mass to charge ratio and afterwards recognised at the detector. For identification of the reaction products the downstream mass spectrometer is used.[48,49]

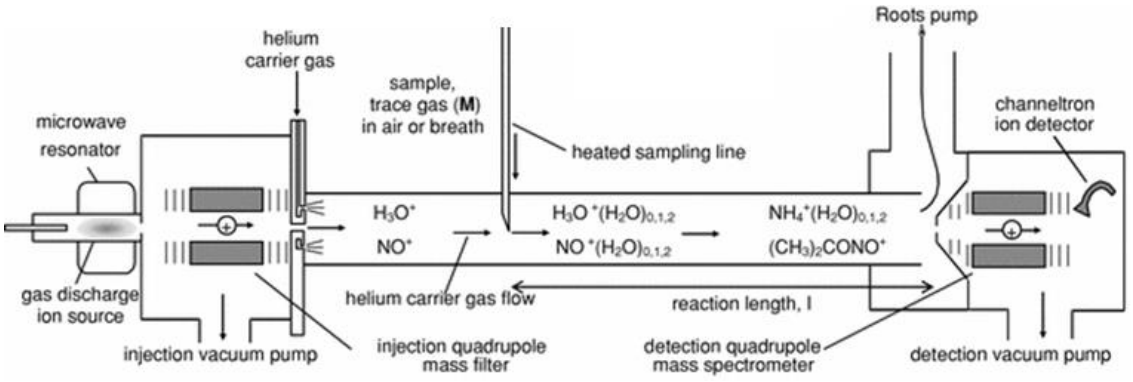

Figure 2: Schematic figure of the construction of a SIFT-mass spectrometer.[48]

Other methods for the analysis of gas samples are gas chromatography mass spectrometry (GC-MS). Both techniques can be used to analyse VOCs but have different strengths. Therefore, they complement rather than replace each other. On the one hand, SIFT-MS analyses whole air in real time with typical detection limits at parts-per-trillion level by volume (pptv). Moreover, a very soft and controlled form of ionization is used, leading to very low fragmentation, so no chromatography is required. Because of these factors long-term calibration stability, reduced maintenance and easy configuration of the instrument is possible. On the other hand, the electron ionization (EI) of the GC-MS leads to a stronger fragmentation of the substances and thus more structural information than the softer ionization of the SIFT-MS method. In addition, less volatile substances can also be measured by heating the column. However, SIFT-MS is faster than GC-MS and can also be used with a non-technical background. But, GC-MS provides very good specificity, as it separates the mixture of substances and creates a separate spectrum for each compound but relies on electron impact ionization and chromatographic separation. That is why it is relatively slow, must be operated by skilled personnel and has higher maintenance requirements compared to SIFT-MS. It usually requires preparation or preconcentration of the samples and higher validation effort which leads to the result that SIFT-MS complements the selective analysis of GC-MS with faster screening as well as easy handling.[50,51]

However, in order to illustrate the complexity of the soil, it is not enough to just measure gas emissions and understand their impact on the environment. Other parameters directly related to these emissions also need to be determined. One of these parameters is the redox potential, which provides information about the ion conditions in the soil and can be measured with the aid of electrodes.

1.4 Redox potential

The redox potential is the potential difference between the electrode and the reference electrode (hydrogen electrode). Redox pairs of the electrochemical voltage series always consist of an oxidizing agent which absorbs electrons and a reducing agent which releases the electrons.[52] The tendency to release electrons as well as the reducing power of a substance, is described by the redox potential. The electrons move from the atom of more negative potential to the atom of more positive potential. This force is called ΔE^0, which is related to the change of the Gibbs energy (free enthalpy) of a reaction (cf. Equation 2).[53]

Equation 2: Calculation of Gibbs energy with z: Charge, F: Faraday constant (96.5 kJ/(V*mol), ΔE^0: Change of the Redox potential.

$$\Delta G^0 = -z * F * \Delta E^0$$

If a metal electrode with high electron conductivity gets in contact with a redox environment, a potential occurs in which the electrode represents an electron exchanging surface. This potential can be measured as redox voltage (V or mV) and results from electrons attached on the surface of the electrode during the measurement. If platinum foil is dipped into a solution with trivalent metal ions, the ions devolve to bivalent ions through admission of platinum electrons. Therefore, the surface of the electrode gets positively charged. This happens until the process gets stopped by electrostatic repulsion. The structure of a redox electrode is shown in Figure 3. The potential arising in the solution can then be described through Nernst equation (e.g. Equation 3) in which the redox potential (E_N) is temperature dependent. Nowadays hydrogen electrodes are no longer used as reference electrode because Ag/AgCl or Hg_2Cl_2 electrodes are much easier to handle. But for historical reasons, the redox potential still is related to the potential of the hydrogen electrode with a pressure of p = 1.014E5 Pa and a H^+-activity of 1. For conversion, the measured potential has to be added to the potential of the reference electrode which itself is temperature dependent again.[54]

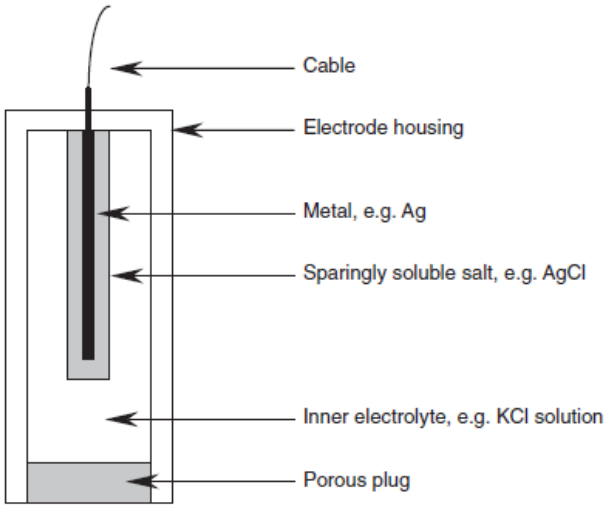

Figure 3: Schematic structure of an Ag/ AgCl redox electrode.[55,56]

Equation 3: Nernst-equation. E_N: Redox potential, E_0: Standard redox potential (T = 298 K, 10^5 Pa, c(ox) = c(red) = 1 mol/l activity), R: Universal gas constant = 8.314 J/(mol*K), F: Faraday constant = 96.484*10^3 J/(V*mol), T: Absolute temperature in Kelvin (K), n: Number of electrons converted, a(ox): Activity (mol/l) of the oxidised form of the substance, a(red): Activity (mol/l) of the reduced form of the substance.[56]

$$E_N = E_0 + \frac{R * T}{n * F} \, ln \frac{a(ox)}{a(red)}$$

To generate energy, microorganisms in the soil use electron transport systems. Electron donors with a high redox potential such as O_2 provide a lot of energy, which is why they are first used for metabolism. Therefore the redox potential in well aerated soils, is closely related to the O_2 concentration.[57,58] Depending on which electron donors are present, the redox potential changes due to their conversion by the microorganisms. Since the soil microorganisms have specialized in the use of different electron donors depending on the species, the redox potential indirectly maps the metabolic processes in the soil. Very low values of redox potential for example, are caused by reducing conditions which are creating living conditions for anaerobic microorganisms. These are then producing reducing substances like H_2S through bacterial sulphate reduction which is again stabilizing the low redox potential. Earlier studies showed that low redox potentials are necessary for initiation of bacterial sulphate reduction. It was also shown, that *Desulfovibrio* organisms largely responsible for reduction of sulphate in soil require a potential of about -200 mV in the medium for the initiation of sulphate reduction.[59] Harter and McLean found out that sulphide formation in soil was very active at a redox potential below -75 mV.[60,61]

Furthermore, low redox potential in reducing sediments and waters is caused by means of typical ions or substances in their lowest oxidation state like iron as Fe^{2+}, manganese

as Mn^{2+}, nitrogen as NH^{4+} or N_2 and sulphur as HS^- or S^{2-}. Even high contents of organic matter can lead to reducing sediments. In stagnant waters and soil oxygen can penetrate the first layers but in deeper regions the environment is getting anoxic. The resulting gradient in redox potential can be measured.[62,63]

The measurement of the redox potential is most reliable in oxigen-deficient environments but are more variable and less meaningful under aerobic conditions.[64] Nevertheless, even in well aerated soils, the redox potential is closely related to the O_2 concentration.[57,58]

However, it is not only the redox potential itself that is interesting, but in particular its connection with VOC emissions from the corresponding soils.

If anaerobic microsites in the soil can be found with the help of gas investigations in which the redox potential is considerably lower than in other places, the reaction spaces in the soil could be better explored. It would also be possible to estimate how many and how large they are, which would provide information about the conditions and metabolic processes in the soil.

1.5 Impact of redox potential in soil on VOC emissions

In previous studies, the influence of the redox potential on the emissions of gases such as CO_2, CH_4 and NO_2 from soils has already been investigated. Many were concerned with agricultural soils such as paddy rice fields as these create conditions for the production of two important greenhouse gases, CH_4 and N_2O.

Therefore, rice paddy soil from Louisiana (USA) was examined under laboratory conditions. Controlled redox conditions between +500 and -250 mV were set, and it was observed that below the critical value of -150 mV the production of methane increased. Other studies have confirmed the area of this critical value, although it differs slightly depending on the type of soil.[65,66] One research report showed a negative exponential relationship between redox potential and CH_4 production between -230 and 150 mV.[67] Furthermore, it was determined, that lower the redox level in the soil leads to higher CH_4 emissivity. Already 50 mV reduction of the redox potential caused a 10-fold increase of the methane emissions in the range of -150 to -250 mV. The highest amount of N_2O evolved during denitrification reactions was measured at a redox potential of 0 mV. It was also observed that the more reducing the soils, the more N gases were emitted, but the smaller the N_2O/ N_2 ratio of the resulting gas.[68]

However, not only agricultural soils were investigated, but also the redox potential and the gas emissions of oxygen (O_2) and three greenhouse gases (CO_2, CH_4, and N_2O) of the profile of a coastal forest. This site is an ideal model for the effects of future sea-level rise on coastal ecosystems. The data were not collected under laboratory conditions as in the other research projects, but in field studies. They showed that a clearly separated boundary between ridge and swamp and redox potentials below +300 mV already led to methane emissions. Thus, the redox values were much higher than in homogeneous soils (-150 mV). The highest N_2O concentrations in soil were measured at a redox potential of +250 mV.[69]

Studies that focused only on the emission of nitrogen oxides from soils investigated samples of the Ap horizon of a Huron soil. The aim was to establish a relationship between NO_3^- and NO_2^- reduction, nitrogenous gas production and redox potential under anaerobic laboratory conditions. It was found that NO_3^- and NO_2^- reduction occur at E_N between 200 and 180 mV. Gas chromatography showed that the denitrification gas was composed of N_2, N_2O and NO. The production of N_2 decreased by decreasing temperatures while NO production increased and NO_2^- production was not significantly affected by temperature. The decreased production of NO at low temperatures when NO_2^- was the nitrogen source was attributed to chemo denitrification processes.[70]

Under laboratory conditions, further research showed the influence of controlled redox conditions (-200, -100, 0, +100, +200, +300, and +400 mV) on N_2 and N_2O emissions. A redox value between +300 and +200 mV was found critical for denitrification to occur, wherein both N_2 and N_2O are formed. The maximum amount of N_2O evolved at a redox value of 0 mV, whereas dinitrogen emissions were only measured at lower redox values. The highest N_2/ N_2O evolution ratio was observed at -200 mV and the ratio decreased with increasing redox. A lack of N-balance during denitrification at redox levels of +100, and +200 mV is also reported.[71]

These already available studies show that the redox potential is clearly related to the production of N-gases and methane. Since these also have an influence on the climate, cause acid rain and contribute to the understanding of complex processes in the soil, these substances and their production in the soil also need to be better investigated.

1.6 Soil conditions at the Schlöppnerbrunnen fen

There are different types of soils, which differ in their structure and composition. One of them are peatlands which are poorly drained areas that are periodically or permanently water saturated.[72] They are important to the global carbon cycle because they store approximately 30% (i.e. 450 Gt) of the terrestrial carbon reserves.[73,74] One of these peatlands is the Schlöppnerbrunnen fen which is slightly acidic and contains a lot of iron (Fe). It has been found out, that the majority of this soluble Fe(II) and Fe(III) is complexed to dissolved organic matter (DOM) (cf. Figure 4). These complexation with organic matter and water-extractable organic matter (WEOM) influences the accessibility of iron species for microbial processes because it depends on solubility and redox state.[75]

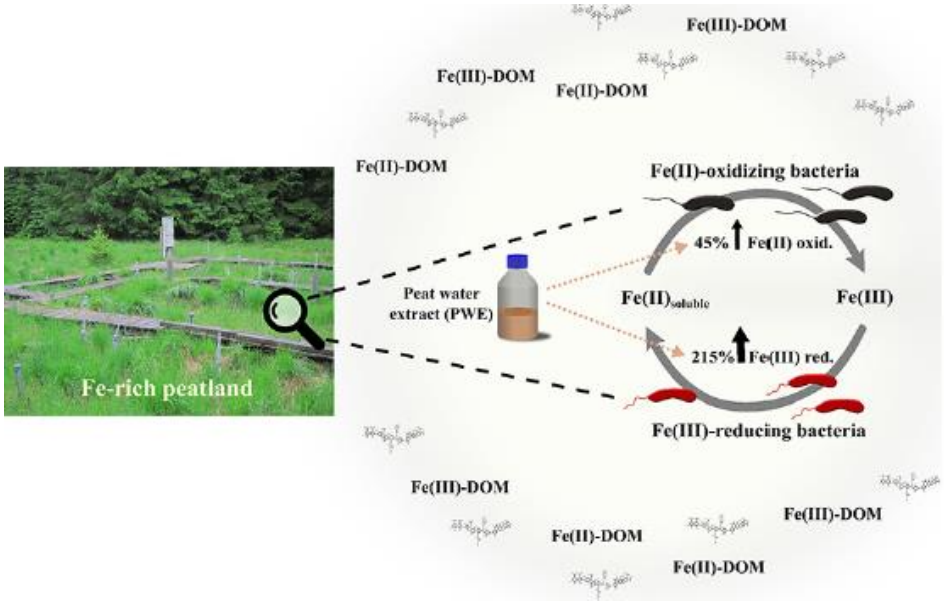

Figure 4: Oxidizing- and reducing- processes in the Schlöppnerbrunnen fen.[75]

Since not only the iron but also the water content influences the produced VOCs through its impact on microbial activity and diffusion, this must also be considered. Dehydration and remoistening of the earth causes fluctuations in the gas exchange between the peat soil and the atmosphere. Previous studies investigated the vertical distribution of CO_2 and CH_4 and their response to dehydration as well as temperature effects and different drying intensities. It was found that shorter drying events under warm conditions favour CO_2 production. The regeneration time of methane production after drying is influenced by temperature, drying intensity and duration and increases with extending dryness. However, warm conditions favour the regeneration time of methane production with enough humidity.[76,77]

A major source of this CO_2 and methane production in peatland soils is the degradation of cellulose by soil organisms such as fungi and bacteria. Earlier studies dealing with CO_2 production in peatlands by degradation of cellulose found that this takes place via mineralisation in the first few oxic centimetres of soil.[78,79,80] Since most layers of flooded peatland soil are anoxic, the cellulose is hydrolysed to soluble celludextrin, cellobiose or glucose by cellulase systems (cellulosomes) of cellulolytic fermenters.[81,80] In the absence of alternative electron acceptors (e.g. sulphates, nitrates, oxidized iron and oxidized manganese), secondary fermenters convert reduced fermentation products such as butyrate, propionate and ethanol into methanogenic substrates such as acetate, formate, molecular hydrogen and CO_2. Methanogens then convert them into methane and CO_2, which is the final step in the anaerobic mineralization of the organic matter.[82] Therefore, peatlands and other wetlands are producing 23–40% of globally emitted methane and are important sources of the greenhouse gas methane.[73,83,84]

2 Objective

The aim of the work was to relate the chemical composition of the soil, its gas emissions and the redox potential to each other and to investigate different parameters such as water content, soil depth, oxic and anoxic conditions. In particular, the relationship between the VOC emissions of the soil and the prevailing redox potential should be explored. In addition, this relationship should be used to investigate whether uniform conditions in the soil can be established during certain incubation conditions or whether different micro spaces can be detected. Furthermore, conclusions should be derived about metabolic and chemical processes in the soil based on the measured emissions and redox potential, as well as the ion chromatographic data, in order to illustrate and understand the complex chemical, ecologically relevant processes in the soil.

3 Methods and materials

3.1 Site description

This soligenous fen of less than 1 ha is surrounded by a Picea abies forest and has already been described in previous work. It lies in the Fichtelgebirgsregion in the northeast of Bavaria (50°07′55″N, 11°52′52″E) at an altitude of about 750 m above sea level and is mainly covered by vascular plants such as *Mollinia caerulea*, *Carex rostrata*, *Carex canescens*, *Juncus effusus*, *Nardus stricta* and *Eriophorum vaginatum*. Until 1950 the region underwent peat extraction for glasswork.[76,77] The intermediate sites are covered with sparsely found *Sphagnum spp.* patches or are covered with rotting litter of vascular plants. The annual precipitation was 1156 mm (1961-1990) with a temperature of 5 °C. The water level varies between 5 cm and 15 cm below peat surface for 50 % of the year and was only 5 % of the year 2008-2009 above a depth of 5 cm. In summer the water level even dropped to 70 cm below the surface. The two different sampling sites "C" and "M" are located in the Schlöppnerbrunnen II (SB II) fen and have different Iron and water contents. The iron content of both sites is quite high, but the iron and water content in site "M" is slightly higher than in site "C", since the terrain is slightly sloped towards site M.[76,77]

3.2 Soil parameters

The weather at the SB II field site on the day of sampling (16.05.19) consisted of drizzling rain and a temperature of approx. 10°C. Soil samples with lower iron content and with higher iron content were taken. From both sites disturbed samples of 2-10 cm and 10-20 cm were taken by digging a large core with the spade and separating the fractions from each other. The samples were placed in PE bags. The air was pressed out of the bags and the samples were stored at 4 °C during transport and parts of the soils were air-dried in the laboratory later.

For the oxygen free incubation experiment (cf. 3.5.2 Oxygen free incubation experiment) 18 soil cores were taken later (25.09.19) with the Pückelheimer corer. These came from the sampling site with high iron content (site "M") from a depth of 0-30 cm and were packed in PE bags, the air was pressed out and they were stored at 4 °C during transport. The weather was cloudy to sunny at a temperature of about 18 °C. In addition, pore water was taken from a depth of approx. 1 m and filled into previously autoclaved

(Autoclav Systc DX45, Systec GmbH, Germany) glas bottles (250 ml, Schott bottle Duran®, DWK Live science GmbH, Germany).

3.2.1 pH extraction

Both Millipore water and a 1 M KCl (CAS: 7447-40-7, Merck KGaA, Germany) solution were used to extract the soil samples. Subsequently, 5 g +/- 0,05 g soil sample were extracted with 25 ml extraction solution in an overhead shaker (Reax20, Heidolph Instruments GmbH & CO. KG, Germany) for 1 h each. Afterwards, the slurry incubated for 1 h, the supernatant was decanted, and the pH value was determined using a pH electrode (pH Meter 538 MultiCal®, WTW, Xylem Analytics Germany GmbH, Germany). The pH electrode was first calibrated with buffer solutions (pH 9.180 and 4.006) (PL9 & PL4, Xylem Analytics Germany GmbH, Germany) rinsed with Millipore water and then immersed in the extraction solution. For the pH extractions of the oxygen free incubation experiment (see 3.3.2 Oxygen free incubation experiment), 10 g wet soil were extracted with 50 ml Millipore water.

3.2.2 Nitrate /Nitrite extraction

The nitrate and nitrite content wa determined by weighing three replicates of 5 g +/- 0.05 g soil each into 50 ml reaction vessels. The extraction agent was a KCl solution (2 M), which had been prepared before. Subsequently, 50 ml KCl (aq.) was added to each sample and the samples extracted for 1 h while shaking. The extraction solution was then filtered into a new reaction vessel using a paper filter (foldet filters 185 mm, Wartman^{TM}, GE Healthcare Europe GmbH, Germany) rinsed with Millipore water and a small quantity of sample. The extracts were stored in the freezer (Freezer LGUex 1500 Index 22B /001, Liebherr-International Deutschland GmbH, Germany) at -20 °C until the nitrate content was measured via Flow Injection Analysis (Quikchem QC 8555, Lachat Instruments, Hach Company, USA). For the oxygen free incubation experiment (see 3.3.2 Oxygen free incubation experiment) only one time 10 g +/- 0.05 g soil each were extracted with 50 ml KCl solution (2 M). The extracts were measured by AG Roma (MPI Jena) using Flow Injection Analysis (FIA).

3.2.3 Sulphate extraction

The sulphate content was determined by extraction of three replicates of 5 g +/- 0.05 g soil each with 50 ml $CaCl_2$ solution (0.0125 M) (CAS: 10043-52-4, Merck KGaA, Germany). The extraction batch was then incubated for 1 h while shaking and the su-

pernatant was filtered into a new reaction vessel using a Wartman filter. The extracts were stored in the refrigerator at -20 °C until the sulphate content was measured by ion chromatography (DX 500, Thermo Fischer Scientific GmbH, Germany).

3.2.4 Elementary analysis

For the analysis of the elementary composition of the soil samples, they were first air-dried and sieved to 2 mm. The samples were then finely ground using a ball mill (MM400, Retsch GmbH, Germany) and weighed into ceramic micro vessels with a precision of 240-260 mg. The total and organic carbon and nitrogen content of the samples should then be determined. 400-500 mg WO_3 were added to the samples for the determination of the total C and N content. For the determination of the organic C and N content WO_3 was added to the samples after treatment in a muffle furnace (B180, Nabertherm GmbH, Germany). In addition, two standards (Bodenstandard Nr. 1.1 HE33860100, HEKAtech GmbH, Germany and Bodenstandard 1, IVA Analysetechnik GmbH & Co. KG, Germany) were added in extra vessels. Subsequently, the samples prepared in this way were forwarded to AG ROMA for analysis. The water content was also determined for both sample rows (cf. 3.2.5 Water content determination).

3.2.5 Water content determination

To determine the water content of the soil samples, 5 g of moist soil were weighed in and dried overnight at 40 °C (drying chamber E28, Fa. BINDER GmbH, Germany). Afterwards, they were dried again overnight at 105 °C, to remove the crystal water, which is not accessible to microorganisms, and cooled with silica gel in the Exicator (Exicator GL32, Glaswerk Wertheim, Germany). To determine the dry weight, the soil samples were reweighed after cooling and the water content was calculated from the difference between wet and dry weight.

3.2.6 SIFT-MS measurement

SIFT-MS (Voice 200 Ultra, Syft^{TM} Technologies, NZ) was used to measure VOC emissions using Helium (Helium 5.0, Westfahlen AG, Germany) as the carrier gas and a PVOC-SIFT-MS Standard for validation (PVOC-Standard Scott^{TM} (2 ppm of 1,2,3,4 Tetrafluoro Benzene, Benzene, Isobutane, Octa Fluoro Toluene, *p*-Xylene, Perfluorobenzen and Toluene in Nitrogenbalance), Air Liquide Company, USA). The SIFT-MS Inlet was configured as described in previous studies (vgl. Figure 5).[85]

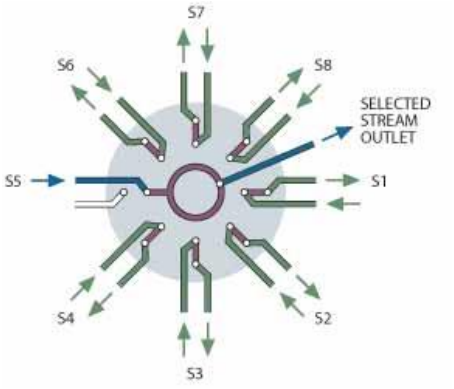

Figure 5: Schematic representation of the sample inlet installed on the SIFT-MS device and its different Ports (S1-S8).

The VOC-free air flow and nitrogen or argon gassing of the soil samples was created by the Pure Air Generator (PAG 003, Eco physics AG, Switzerland) controlled by the Mass flow controller (MFC) (554992 G, MKS Instruments Deutschland GmbH, Germany) or the Gas Flow Control Unit (GCU) (GCU Standard Ionimed Analytics GmbH, Germany) and needle valves (Swagelok® S52-A, Swagelok Company, USA). The flows through the chambers were checked using an Air Flow Calibrator (Gilian® Gilibrator2 primary flow generator sensityne Deha Haan & Wittmer GmbH, Germany). The gases were passed on via PFA Tubes (PFA4X2NATUR, Eisenbarth GmbH, Germany). The SIFT-MS methods used to measure the emissions were called RedoxScreeningS2-S11.sme snd testSoilDMS-s2-s11-long.sme and the chambers were continuously measured one by one. The details of each method are listed in A1 SIFT-MS measurement Table 6 and Table 7.

3.2.7 Redox chambers

The redox chambers were prepared for the experiments by ensuring that the electrodes were clean and that the salt bridges of the reference electrode had the possibility of contact with the soil, buffer or sand. The redox pins were calibrated by one-point calibration with a redox buffer (pH (20 °C) = 7.02 +/- 0.5 and E_H (20 °C) = 228 mV, InLab® solutions redox buffer solution, Mettler Toledo AG, Germany). The specially designed redox chambers (Karl Kuebler, MPI Jena) are consisting of different copper electrodes and an Al/AlCl reference electrode (InLab Reference, Art. Nr. 51343190, Mettler Toledo) which is stored in a 3 M KCl solution connected with the chamber over salt bridges (cf. Figure 6). The experimental setup of the redox measurement with downstream SIFT-MS is shown in Figure 7.

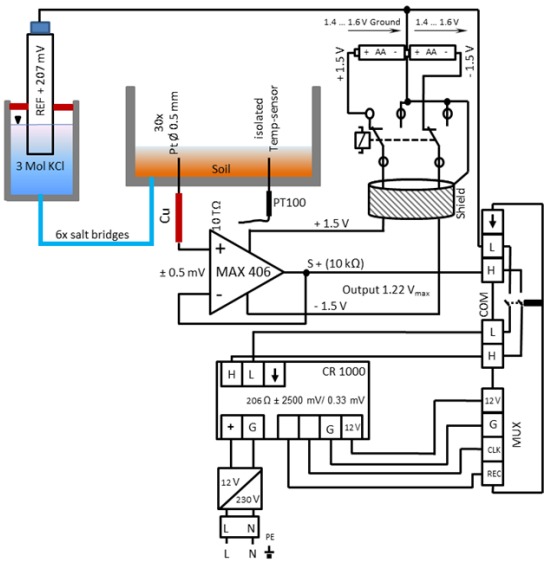

Figure 6: Schematic representation of the structure and function of the redox chambers, simplified by showing only 1 platinum wire electrode and 1 salt bridge connected to a AgCl reference electrode (Mettler Toledo) in 3 M KCl (Karl Kuebler, MPI Jena).

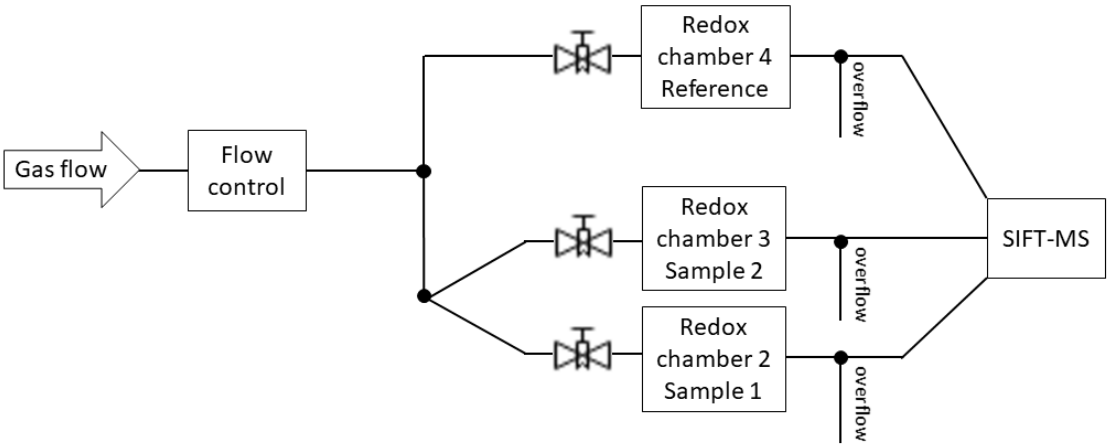

Figure 7: Schematic representation of the experimental setup of the soil samples experiments measured with redox electrodes and SIFT-MS.

3.3 Method development

3.3.1 Pressure experiment

A field capacity of 100 % was set for three soil samples and then measured using SIFT-MS at VOC-free air flow. The triplicates were measured successively at three different pressures (1 bar, 2 bar, 3 bar). This measurement was repeated the next day in reverse order. The fluxes and the amount of used soil are shown in Table 1.

Table 1: Gas flow through every chamber during SIFT-MS measurement and weight of every soil sample in the chambers.

Chamber	Gas-flow in ml/min	Weight in g
2	99.6	32.2
3	102.9	47.7
4	96.1	47.5

This experiment was later repeated with sand and water at a flow rate of 103.0 ml/min. 50 g sand was moistened with 60 ml water and incubated for 30 min under VOC free air flow before the measurement. The emissions were then measured using SIFT-MS at pressures of 1 bar, 2 bar and 3 bar.

3.3.2 Gas flow experiment

100 ml moist soil (SBII 0-10 cm low Fe) and 30 ml dest. water was filled into a 250 ml Schott bottle. The bottle was sealed and fumigated with different gas flows of VOC-free air. Different combinations with the SIFT-MS fluxes were also tested. It had to be considered that the flow in the chambers is always higher than the one into the SIFT-MS device. The different flow combinations are shown in Table 2.

Table 2: Listed gas flows through the bottle and into the SIFT-MS device.

Gas flow into SIFT-MS in ml/min	Gas flow through Schott-bottle in ml/min					
50	100					
60	100	110				
70	100	110	120			
80	100	110	120	130		
90		110	120	130	140	
100			120	130	140	150

3.3.3 Flow fluctuation experiment

A redox chamber was filled with moist soil, checked for leaks, connected to the gas flow, incubated for 30 min and then measured ten times using SIFT-MS. Thereby the control of the gas flow by means of the MFC was compared with the control by the GCU. The methods used and the equipment for the individual test runs are summarized in Table 3.

Table 3: Conditions and devices used for SIFT-MS measurement.

Soil	Weight in g	Device	Chamber	Gas flow in ml/min
SB II	140,5	MFC	2	309.4
0-10 cm Site M		GCU	2	286.7
No Soil		GCU		330.5

3.4 Preliminary experiments

3.4.1 Soil screening

The soils were first air-dried, and the roots were removed in order to prevent the plant parts from preventing comparability. Afterwards eight replicates of each soil were weighed into a reaction chamber and two each were brought to a specific soil moisture level (Research plus 100 ml pipette, Eppendorf AG, Germany) (cf. Table 4). The soil samples were incubated overnight at room temperature and the water loss was compensated the next day. They were then incubated for 30 min at 20 °C at VOC-free air flow before being measured by SIFT-MS. For each Water Holding Capacity (WHC) a control with the same amount of sand (CAS: 14808-60-7, Sea sand acidic washed, Fischer scientific GmbH, Germany) and water content was measured. The VOC free air flow through each chamber was approximately 100 ml/min +/- 7 ml/min.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated for the presentation and evaluation of the results and inserted into the figure as horizontal line. The LOD represents three times the standard deviation (mixing ratio of the control). The LOQ is calculated by multiplying the standard deviation (mixing ratio of the control) with ten.

Table 4: Specific conditions of each soil sample.

Soil	Weigh in g	WHC in %
SB II	18,5 (each)	30
0-10 cm Site M		60
		100
		150
SB II	19,4 (each)	30

Soil	Weigh in g	WHC in %
0-10 cm		60
Site C		100
		150
SB II	14,8 (each)	30
10-20 cm		60
Site M		100
		150
SB II	22,1 (each)	30
10-20 cm		60
Site C		100
		150

3.4.2 Comparison of oxic and anoxic conditions

In order to measure the Redox potential and the VOC emissions, 2 x 150 g moist soil (SBII 10-20 cm high Fe) was dried under N_2 or VOC free air (500 ccm) flow. Subsequently, the boxes were closed and checked for leaks (device). A chamber flow of 500 ml/min each could then be set via needle valves and MFC. The chamber flow was reduced to 300 ml/min after two days in order to increase the intensity of the SIFT-MS signal. The calculation of the flow to display the diagrams in 4.2.3 Comparison of oxic and anoxic incubation conditions is shown in Equation 4. The data, which could be recorded over a period of two weeks, were evaluated with the help of Excel (Microsoft office) and R (R studio version 3.5.0).

Equation 4: Calculation of the substance flux. Φ: flux of the substance (mol/h), χ: mixing ratio (ppb), ϕ: gas flow (l/h), V_m: molar volume (l/mol).

$$\Phi = \frac{\chi * \phi}{V_m}$$

3.4.3 Incubation time experiment

Three chambers were filled with 105.6 g moist soil (SB II Site C 0-10 cm) and brought to 50 % field capacity (20 ml dest. water). As control another chamber with 105.6 g

sand and the same amount of water was used. These preparations were then incubated in the refrigerator for 24 h with a VOC free air flow of approx. 101 ml/min +/- 11 ml/min and measured by SIFT-MS during this time. The same experiment was then repeated with previously dried soil to ensure the reproducibility of the experiment. For the second repetition of the experiment, four chambers were filled with 33.85 g earth (100 % WHC and 50 % WHC). Two chambers were filled with sand to control the emissions of the soil (SB II Site C 0-10 cm). The preparations were incubated for 24 h in the refrigerator with VOC free air flows of approx. 110 ml/min +/- 9 ml/min while the emissions could be measured by SIFT-MS. The flows of VOC free air through the chambers was approx. 100 ml/min.

3.5 Main experiments

3.5.1 Drying experiment

Three drying experiments with different start humidities were carried out. Before this, the pH value and the water content of the soil (SBII Site M 10-20 cm) were determined (cf. 3.1.1 pH extraction and 3.1.5 Water content determination).

To find out how the emissions in differently flooded soils behave during drying out, the chambers were then filled with soil, the appropriate amount of water was added, and the chambers were sealed tightly. After connecting the gas (N_2) and adjusting the desired flows, the soil was incubated for 1 h under gas flow. Afterwards the redox potential and emissions were measured (SIFT-MS).

The first drying experiment (A) was carried out with 2 x 127.24 g soil and sand and ran for 11 days. In the beginning 15 ml of water were added to the soil. The sand was moistened with 80 ml water because it dries out faster, which could falsify the control measurement. The gas flow was controlled by the MFC and set to 300 ml/min.

The second experiment (B) ran for 12 days. 2 x 131 g moist soil was prepared with 50 ml water, but this time, three times autoclaved soil was used as control. In addition, the gas flow was slightly lowered to approx. 200 ml/min in order to see more VOC emissions and controlled through the GCU.

3.5.2 Oxygen free incubation experiment

To prepare the experiment, the earth cores were pooled and well mixed. Afterwards, the earth was filled into 250 ml Schott bottles (approx. 120 g per bottle cf. A5 Oxygen free

incubation experiment Table 10). Then, 100 ml of pore water were added to the soil. Then nutrient solution (1 M glucose, 1 M lactase, 1 M acetate) of 60 µl (1:1:1) was added and the reaction mixtures were flushed with argon for 1 h. Five samples were then autoclaved and used as reference at one time each.

At intervals of one week each (1-5), five incubation preparations and one autoclaved control sample were sampled destructively. Until then, they were stored at 20 °C in the dark. 40 ml of the headspace was first transferred into GC vials (Fisherbrand™ Headspace-vial (40 ml), Thermo Fischer Scientific GmbH, Germany) using a syringe (Omnifix® 50 ml, B. Braun Melsungen AG, Germany) and then measured Gas chromatography (GC) (Nexis 2030 GC BID Detector, Shimadzu Deutschland GmbH, Germany). Pure Argon was measured as reference value (T0). Then the bottles were incubated under argon flow for 30 min before the gas emissions were measured by SIFT-MS (cf. table with flows and weights). 120 g wet sand (100 ml dest. water) was used as a control. The redox potential was determined by placing the soil on the electrodes of the redox chambers used in the drying experiments. At times T4 and T5, a portable redox electrode (GMH 3500 Series, GHM Messtechnik GmbH GHM Group Greisinger, Germany) was also used. Since the mV_H setting was used to automatically convert the measured values to the hydrogen electrode, this no longer had to be done manually afterwards. Subsequently, a pH extraction and measurement were performed from each soil sample, as well as a sulphate extraction and a nitrate/nitrite extraction (cf. 3.1.2 NO_2^- / NO_3^- extraction and 3.1.3 Sulphate extraction). Moreover, the nitrite content was determined colorimetrically (Spectroquant® Colorimeter Move100 and Nitrite Test, Merck KGaA, Germany). In addition, the samples were prepared for elemental analysis to determine the total and organic carbon and nitrogen content by AG Roma (cf. 3.1.4 Elementary analysis). Furthermore, the water content was determined for each sample. An overview of all samples as well as measured parameters (water content, weight, soil temperature and redox potential) are shown in A5 Oxygen free incubation experiment Table 10.

4 Results

The results described in the following section show the outcome of the measurements and the conclusions of this work from the method development over the preliminary experiments, for the optimization of the test conditions, up to the main experiments with whose help the main hypotheses should be answered.

For the VOC emissions shown in the results, such as DMS 19/63, the first number (19) describes the precursor ion, which ionizes the substance being measured. 19 stands for H_3O^+, 30 for NO^+ and 31 for O_2^+. The second number describes the mass of the substance after ionization in g/mol, which is used to identify the VOCs in the mass spectrum.

4.1 Method development

First, the influences of various parameters such as pressure, flow and flow fluctuations on the measurement, methods used and their results, were investigated in order to find the optimum conditions for subsequent experiments and possible sources of error.

4.1.1 Pressure experiment

The hypothesis to be tested in this experiment was, that the pressure has an influence on the solution of VOCs in the gas phase and therefore fewer VOCs can be measured if the pressure in the chamber increases. The data from earlier measurements suggested, the soil emits only few VOCs. It was assumed that this could be due to the high internal chamber pressure. Although the overflow is supposed to prevent this, the diameter of its tube could be too thin to completely compensate the overpressure. Therefore, it should be checked to what extent the chamber pressure affects the emissions of the measured emissions.

The DMS emissions of three replicates were measured ascending from 1 bar-3 bar (cf. Figure 8 (left) Replica 1,2 and 3) and afterwards descending from 3 bar-1 bar (cf. Figure 8 (left) 4,5 and 6). The experiment was then repeated with two replicas to check the results (cf. Figure 8 (left)).

When looking at the course of the DMS emissions depending on the chamber pressure, it becomes apparent that the emissions decrease with increasing pressure. That this is not the case becomes clear if the order of the measurement is taken into consideration. When the order of the measurements is considered both experiments show that the emissions decrease in the order of the measurements regardless of the chamber pressure (cf. Figure 8).

This leads to the assumption that the chamber pressure in the range between 1 bar-3 bar has only little influence on the solution of the VOCs in the gas space of the chambers. The initially higher emission values could be related to the remoistening of the soil and the associated activation of microbial metabolism and sudden production metabolites. Substances already bound in the soil could also be released by beeing previously dissolved in the water.

For further experiments it can be concluded that pressure fluctuations have no significant influence on gas emissions as long as they are in the range between 1 bar-3 bar. Also, the pressure in this range can be freely selected for the execution of the experiments without falsifying the results of the gas analysis.

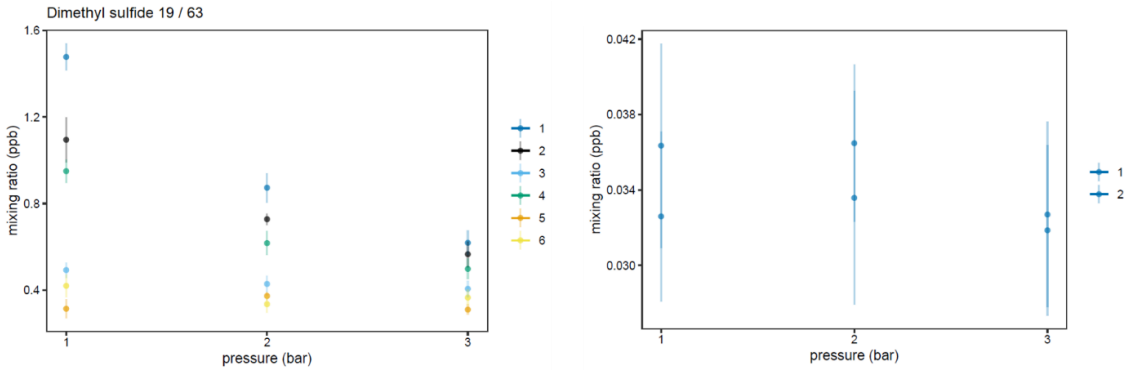

Figure 8: Course of the DMS emissions of both experiments depending on chamber pressure. 1-6 (left): Replica 1-6 pressure experiment 1, 1-2 (right): Replica 1-2 pressure experiment 2.

4.1.2 Gas flow experiment

The gas flow experiment is based on the assumption that the flows in the chambers, the flow of gas phase into the SIFT-MS, as well as their relationship to each other has an influence on the intensity of the signals.

An increased gas flow with constant emissions results in less time for the dissolution of the VOCs in the gas phase and therefore a lower concentration of VOCs can be measured. In addition, a lower flow into the SIFT-MS results in less measurement. Therefore, an optimal ratio between the two flow settings should be selected to measure the emissions. It should also be ensured that the flow into the SIFT-MS device is not higher than the flow through the chambers because this results in a vacuum which in turn leads to false measurements.

For these Investigations the water peak was chosen. This was the case because the emissions from the water are determined by a distribution equilibrium between water and gas phase and are therefore constant. They are more suitable than the VOC emissions

from soil, where the distributional equilibrium is negligible compared to the metabolic changes of the microorganisms. The emissions are thus subject to larger fluctuations which can falsify the results of the flow analysis.

Figure 9 shows the intensity in counts per second (cps) on the y-axis and the flow into the SIFT-MS and the gas flow through the chambers in ccm on the x-axis. As can be seen in Figure 9, the detectable humidity increases depending on gas flow through the chamber and gas flow into the SIFT-MS device. The flow into the device has a much higher influence on the measured emissions than the flow through the chambers.

Therefore, a flow of at least 200 ccm (ml/h) through the chambers was selected for in order to select a higher flow into the SIFT-MS and measure more emissions. A higher gas flow through the chambers was not chosen as this would accelerate the drying of the soil too much due to the increased removal of the water and could build up too much pressure in the chamber.

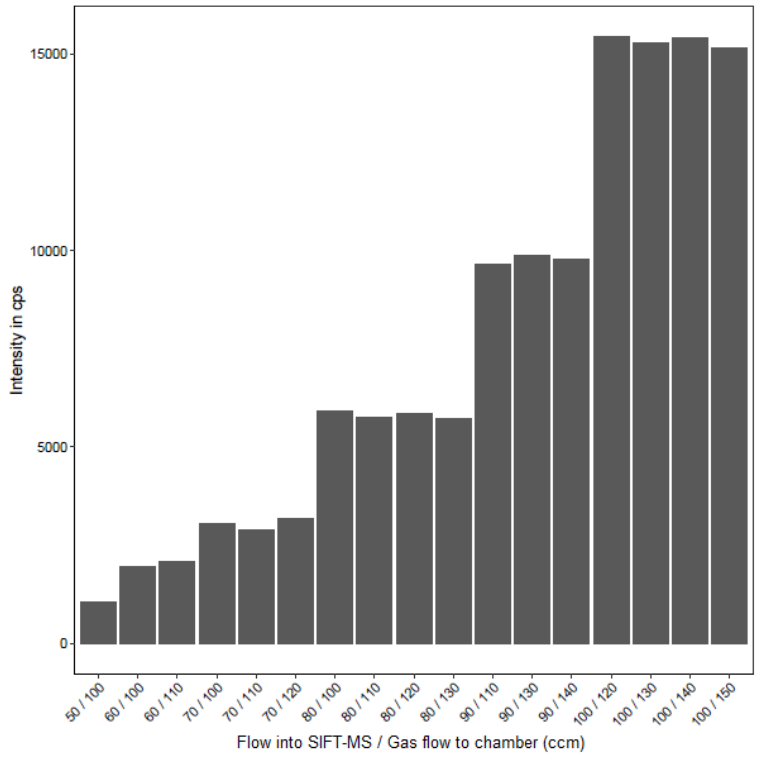

Figure 9: Water emissions of moist sand as a function of gas flow into the chamber and flow into the SIFT-MS.

4.1.3 Flow fluctuation experiment

As previous experiments have shown, during longer SIFT-MS measurements individual measurements failed more frequently. Therefore, the error should be localized in order

to correct it before other experiments. At first it was assumed that the measurement failures were caused by strong fluctuations of the gas flow.

To check the two conditions (chamber and no chamber intermediary) and gas flow control devices (GCU and MFC) were tested in order to see if high gas fluctuations occur and if they are leading to measurement failures. Figure 10 shows that there is no direct correlation between the measured value fluctuations and the used gas flow regulation devices (GCU or MFC).

In order to locate the error, the generated data of the measurement were examined, and it turned out that no emissions were measured at all during faulty measurements. This confirmed the conclusion that the gas flow was not responsible for this, since even with lower gas flows, emissions could be measured, but these would not always be completely absent. In consultation with SIFT-MS experts of the company, the modified SIFT-MS inlet could be identified as the most likely source of error (cf. 3.2.6 SIFT-MS measurement). The SIFT-MS switches alternately from one sample to the next during longer measurements of different samples which may leads to incorrect switching from time to time, so that the port remains closed and no emissions can be measured. Since the Inlet could not be repaired within the time of this thesis, the faulty measurements were removed from the graphics in order to evaluate these.

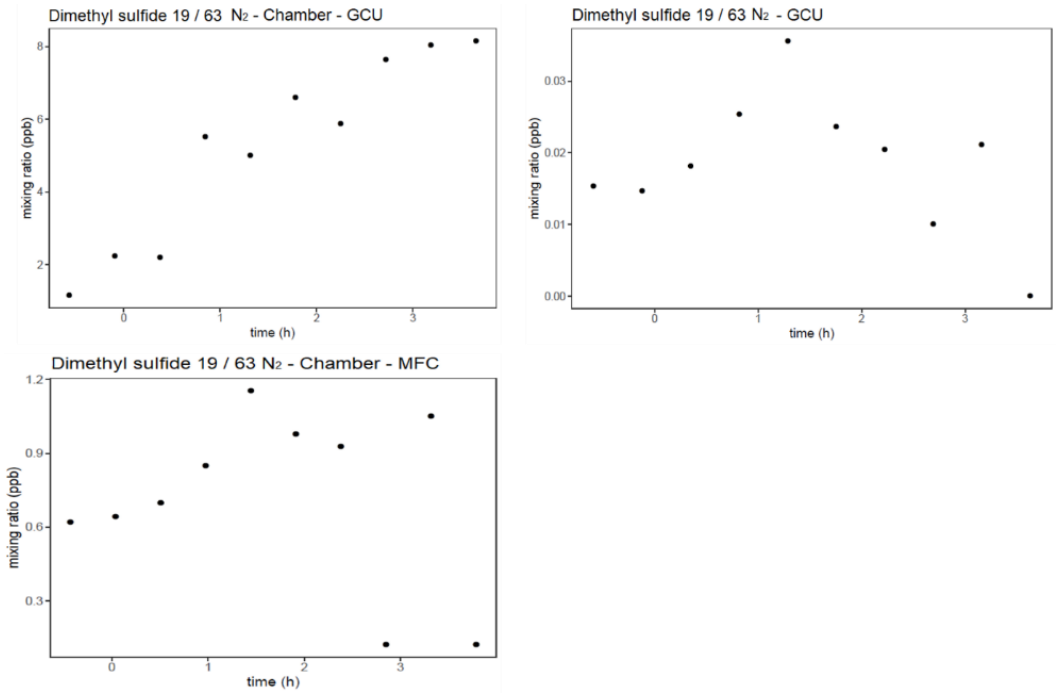

Figure 10: Comparison of the flow fluctuations depending on the used gas flow device.

4.2 Preliminary experiments

After the development of the methods, two preliminary experiments were carried out to test how the emissions and redox potentials of the different soil samples behave under different incubation conditions and to identify the optimal conditions for later experiments.

4.2.1 Soil screening

To check if there are differences in the VOC emission between the soils (Site “M”/ Site “C”) and the soil depth, these were investigated by SIFT-MS measurements. The influence of soil moisture should also be determined. Thereby the emissions of two replicates and one control (dist. water on acid washed sand) were measured by SIFT-MS.

In addition to the VOC emissions, the pH values of the different soils were determined to see the initial, natural conditions of the soil. The soil samples from site "M" showed a slightly lower pH value of pH = 4.07 and the soil samples from site "C" showed slightly higher pH values of 4.08 and 4.18. The pH value of the soil from site "M" that had not been dried before was also slightly higher than that of the dried soil samples and was at pH = 4.11. There were only slight pH differences between all samples, and they are all in the acidic range (cf. Table 5).

Table 5: pH-values of the different Schlöppnerbrunnen soils in H_2O or KCl.

Sample	Weight in g	Solvent (H_2O or KCl) in ml	pH (H_2O)	pH (KCl)
SB II 0-10 cm Site M	5	25	4.07	3.16
SB II 10-20 cm Site M	5	25	4.07	3.30
SB II 0-10 cm Site C	5	25	4.08	3.29
SB II 10-20 cm Site C	5	25	4.18	3.31

Sample	Weight in g	Solvent (H_2O or KCl) in ml	pH (H_2O)	pH (KCl)
SB II 10-20 cm Site M (wet soil)	5	25	4.11	3.56

The evaluation of the SIFT-MS measurements showed that the soils emit DMS, acetone, propanal and methanol, as well as formic acid and pyruvic acid (cf. Figure 11 - Figure 16). If one compares the dimethyl sulfide 19/63 emissions at different soil moisture levels, it becomes apparent that they all follow the same dynamics. The emissions are higher at soil moisture levels of 30 % and 60 % WHC and decrease again with increasing water content. If the individual soils are compared, it is noticeable that they also differ from each other in terms of emission quantity. Emissions of DMS are highest at a lower iron content and a depth of 0-10 cm (SB II 0-10 cm Site "C"). Emissions are lower with a higher iron content and deeper sampling.

Site “M” emissions at both soil depths are approximately 0.03-0.04 ppb. The values of the soil depth 0-10 cm in site “M” are clearly above the limit of detection (LOD) and limit of quantification (LOQ) limits, which, in contrast to the soil depth of 10-20 cm, speaks for a better quantifiability of the DMS emissions. The measurement of soil depth 10-20 cm of site "C" also shows DMS concentrations of max. 0.03 ppm. In comparison to the soil depth 0-10 cm of site "C" these are also closer to the LOD and LOQ values. With maximum values of approx. 0.075 ppb, the measured values of the SB II 0-10 cm site "C" sample are additionally the highest of the four samples and lie far above the determination limits (cf. Figure 11).

If one compares the emission curves of DMS 19/63 with those of DMS 30/62 and 32/62, DMS 30/62 shows the same emission curves with only minor differences. Only the emissions of soil depth 10-20 cm site "C" are much closer to the determination limits and at 30 % WHC even between LOD and LOQ, which is why they are not quantifiable (cf.3.2.6 SIFT-MS measurement). DMS 32/62 also shows this emission pattern. With the sample 10-20 cm Site "M" the measured values lie even more clearly between the LOD and LOQ value.

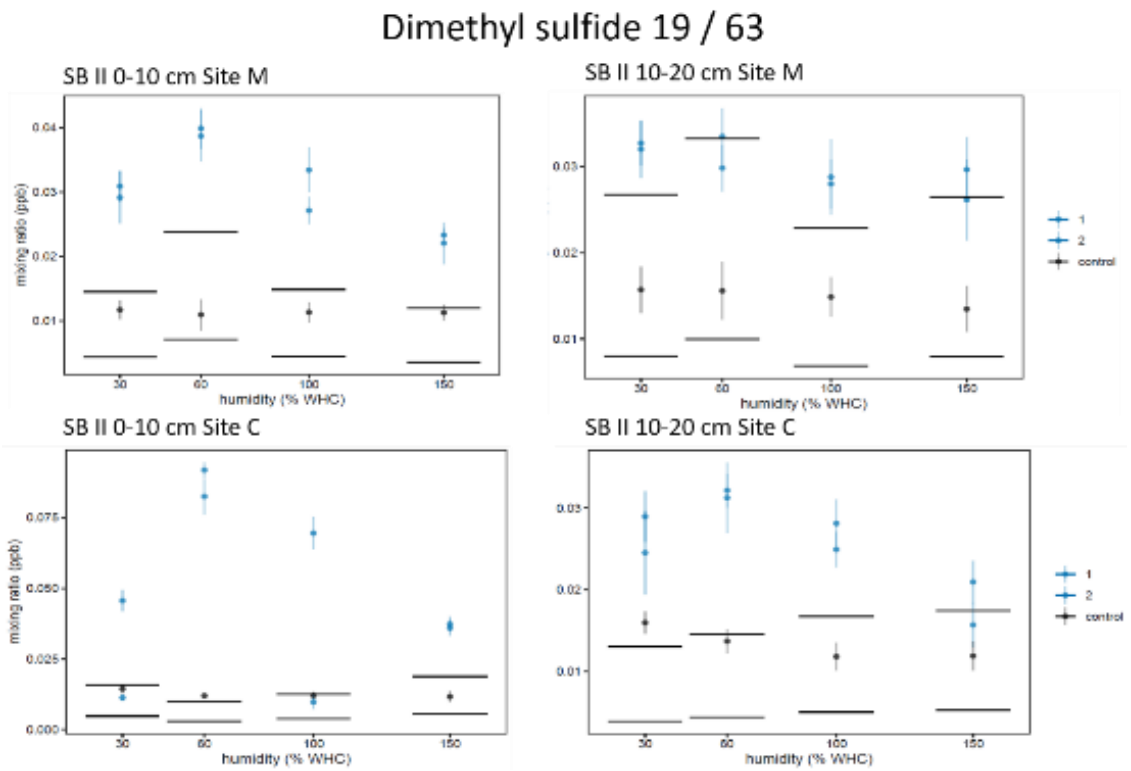

Figure 11: Comparison of dimethyl sulfide emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

Most emissions of acetone 32/43 can also be seen at 60 % WHC. However, this trend only occurs with the more ferrous site "M", whereas site "C" shows a reduction of acetone emissions at 60 % and 100 % WHC. In contrast to the DMS emissions, the highest values of measured acetone occur at high iron content of site "M". Furthermore, the values of the two soil depths in site “M” do not differ from each other. However, in site “C” at a depth of 0-10 cm, very high emissions are visible which surpass the others by far. However, the remaining measurements of this soil depth are in the same range as those of the other sites and soil depths. The values of site "M" in both soil depths are far above the LOD and LOQ limits, which indicates good quantifiability. The measurements of site "C" are closer to the two limits. The two too high measured values of site "C" of soil depth 0-10 cm are unrealistically high, since they exceed all other measured values by about ten times. Furthermore, the fact that the same phenomenon was measured for propanal in the same sample indicates that these are artefacts (cf. Figure 12).

Propanal 30/57 emissions from the more ferruginous site "M", whose peak is reached at a soil moisture content of 60 % WHC, are also much higher. The highest emission value for site "M" is approx. 3 ppb and for site "C" approx. 0.4-0.6 ppb. As before with acetone emissions, the soil of site "C" emits less propanal. Except for the soil depth 0-

10 cm which, similar to the emissions of acetone (cf. Figure 12), contains two very high values, which are probably artefacts. In addition, the propanal values of site "C" drop significantly at 60 % and 100 % WHC. The LOD and LOQ limits are exceeded at all soil moisture levels only by the measurements of site "M" at a soil depth of 10-20 cm. The values of the soil depth 0-10 cm of this site are, with the exception of the measurement, at 150 % WHC above the two limits. The values of the control sample at the measurement of 30 % WHC are however higher than the values of the soil samples. This indicates that for this sample only the values for 60 % and 100 % WHC can be considered actual emissions (cf. Figure 13).

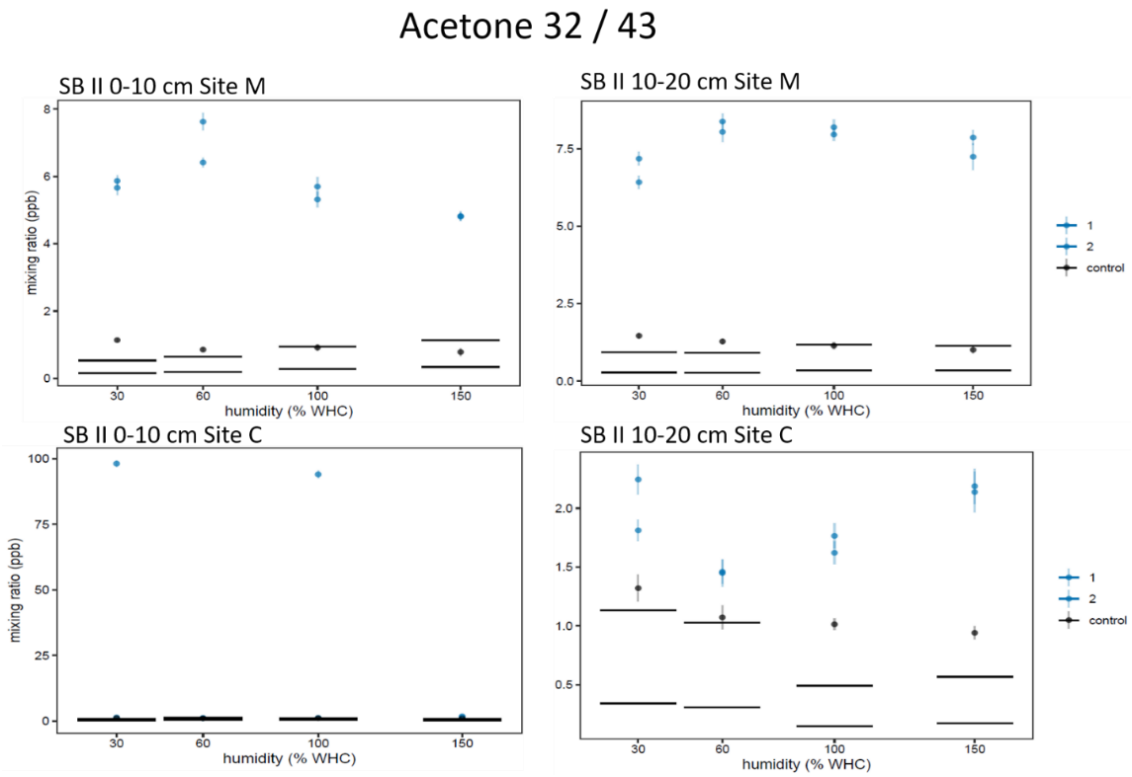

Figure 12: Comparison of acetone emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

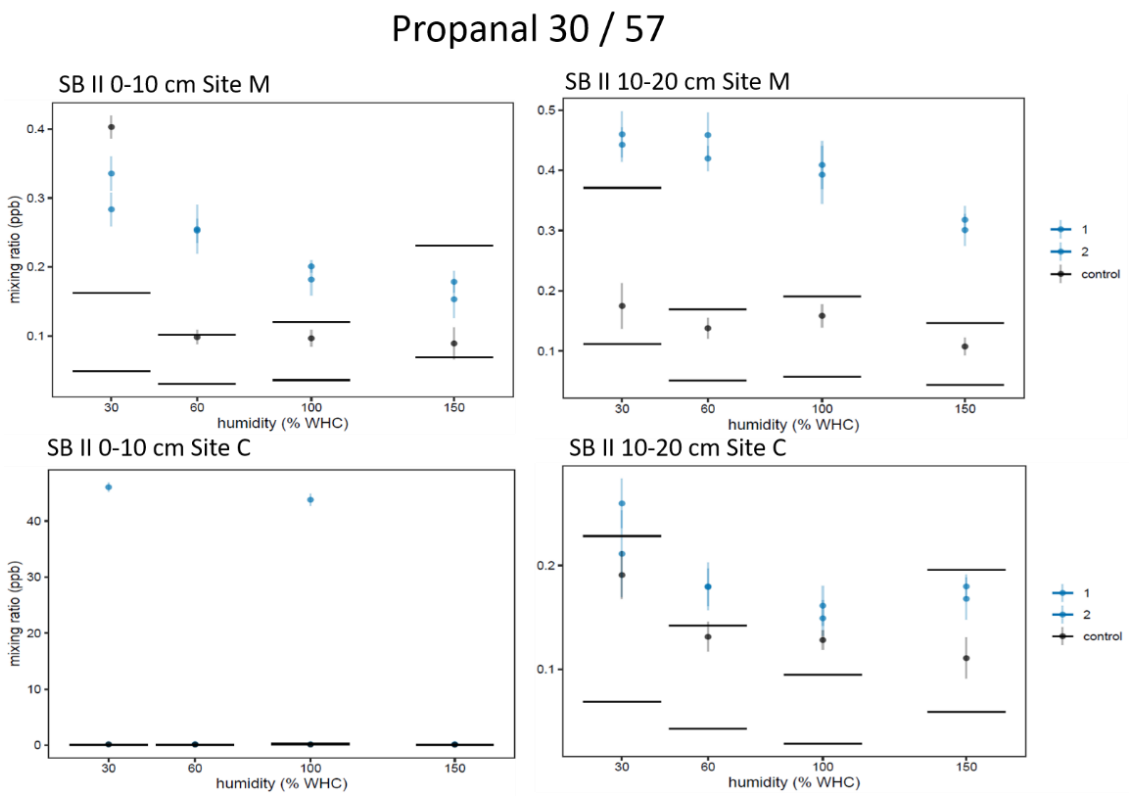

Figure 13: Comparison of propanal emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

Methanol also emits more from the more ferrous soil of the "M" site. The value here is about 1-1.25 ppb compared to about 0.4 ppb for site "C". However, the measured values of the soil samples in site "C" do not differ from those of the control sample and therefore cannot be considered as actual emissions of methanol. In contrast to the other emission dynamics, methanol shows a particularly high emission at a soil moisture content of 30 % WHC in site “M”, which decreases significantly when the soil moisture content increases (cf. Figure 14).

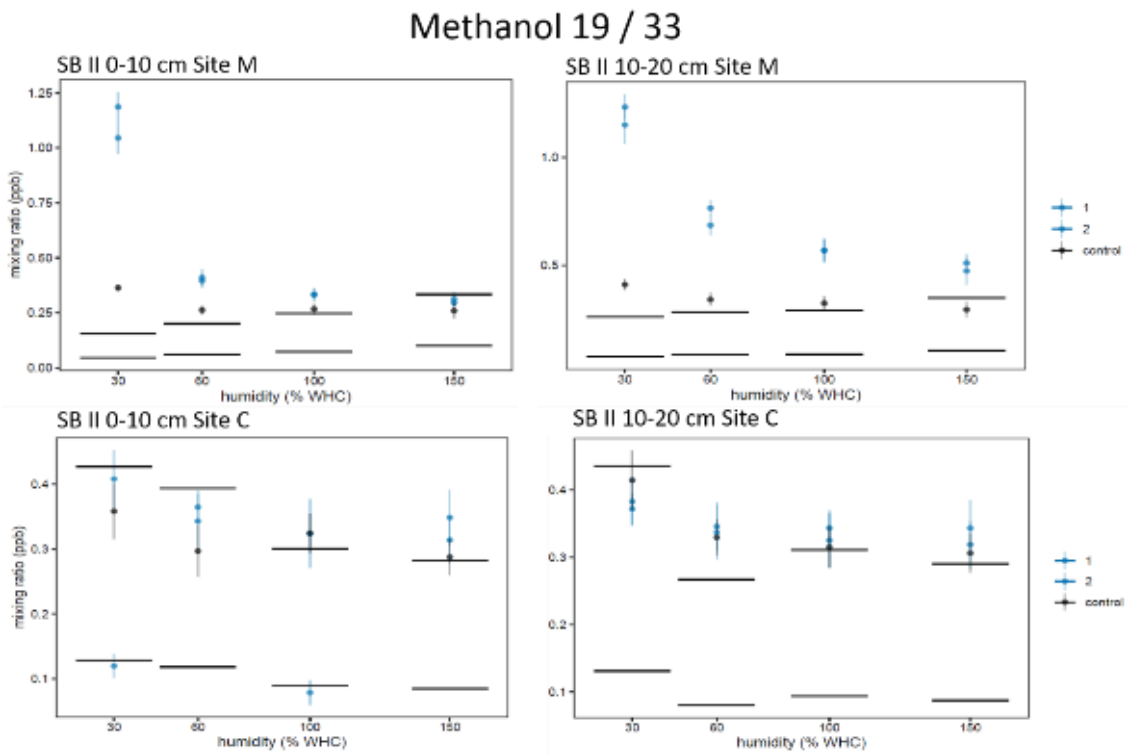

Figure 14: Comparison of methanol emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

If one compares the emissions of the two acids pyruvic acid and formic acid, it is noticed that they all show higher emissions in the more ferrous site "M". They both emit more at a soil depth of 10-20 cm. Pyruvic acid with a value of approx. 2.4 ppb at 30 % and 60 % WHC and formic acid at approx. 0.9 ppb at a soil moisture of 30 % WHC.

The emission values of the soil samples in site "C" do not differ from the measured control values in both soil depths. Furthermore, they are within the LOD and LOQ limits, which makes them non-quantifiable. Site "C" therefore shows no emissions of pyruvic acid or formic acid. In addition, it is noticeable that the emissions of soil depth 0-10 cm from site "C" show two very high measured values, similar to the measurements of propanal and acetone, which are most likely artefacts (cf. Figure 15-Figure 16).

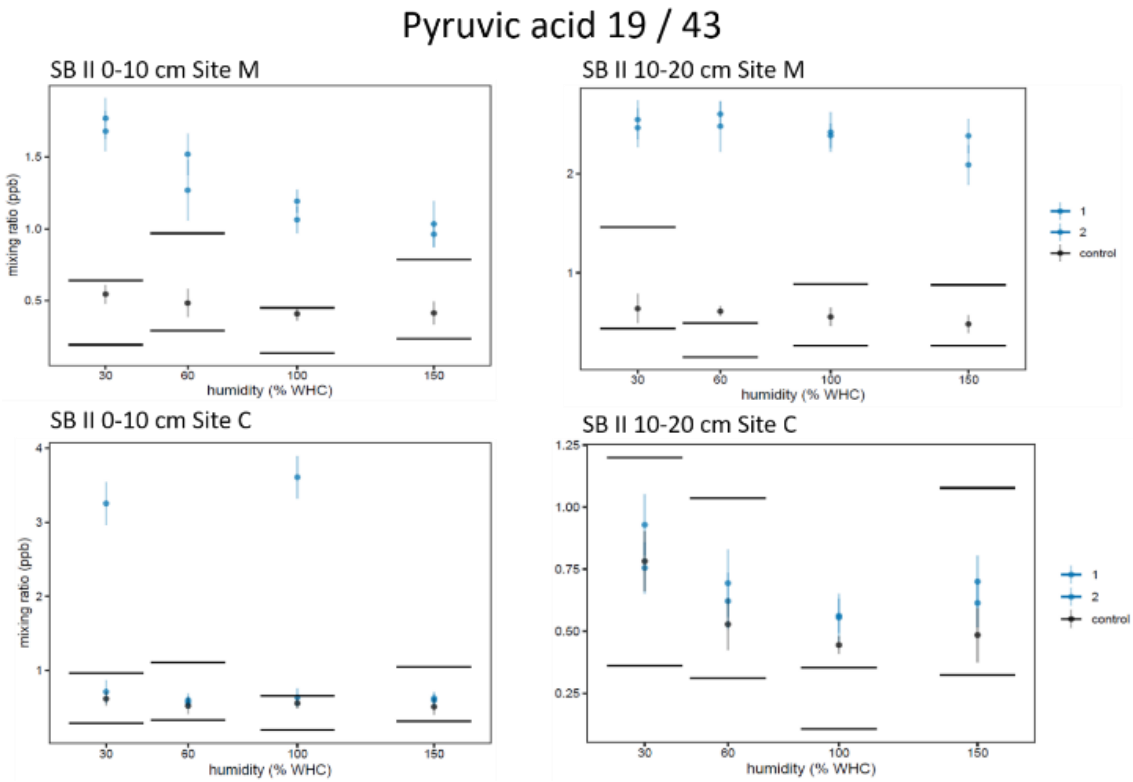

Figure 15: Comparison of pyruvic acid emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

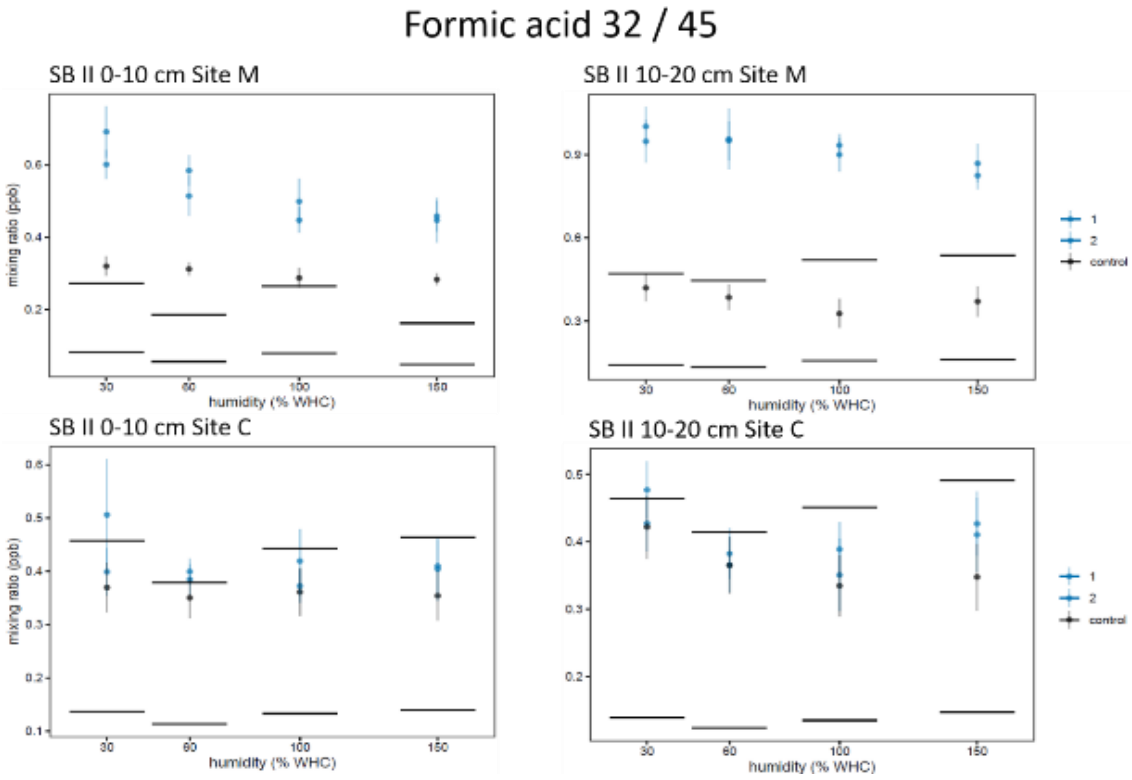

Figure 16: Comparison of formic acid emissions from different soils with different iron and water contents. N = 2 with acid washed sand as negative control, mean +/- 95 % CI. Bars: limit of detection (LOD) and limit of quantification (LOQ).

For all emitting substances, the highest values in soil SB II 10-20 cm Site “M” could be determined. Only the dimethyl sulfide emissions differ from the others, because they are highest in soil SB II 0-10 cm site “C”. A soil moisture of 30 % and 60 % WHC also leads to high VOC emissions in the soil of site "M". Site "C" shows decreasing VOC emissions at 60 % WHC.

This suggests that the higher iron content of the site "M" has an impact on the production of VOCs and leads to higher emissions. Furthermore, the measured values show that the emissions of the soil samples are higher at lower water content (30 %-60 % WHC) than at 100 % or 150 % WHC. This could be due to the fact that moisture favours the growth and metabolism of microorganisms, but too much water inhibits the diffusion of VOCs through the soil and ensures that fewer emissions can dissolve in the gas phase during the same time.

These results led to the use of the soil SB II 10-20 cm site "M" for further experiments due to its high emission values.

4.2.2 Incubation time experiment

The assumption that different incubation times due to delays in the measurement of soil samples using SIFT-MS have an influence on the result should be investigated. In order to exclude the possibility that the graphs show a random course (cf. 4.2.1 Soil screening), because the samples were measured in the order of humidity, the gas emissions were measured after remoistening the soil. In addition, the effects of re-humidification of dried soil samples on the dynamics of VOC emissions during anoxic incubation should be investigated.

Figure 17 shows that DMS emissions increase strongly within the first 5 h after rewetting and peak after about 8 h. The emissions then decrease again until they reach their initial values after 24 h. The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic (cf. 4.1.1 Pressure experiment). This shows that after re-moistening the soil, the emissions already reach an initial peak after approx. 5-10 hours.

But in the experiment 4.2.1 Soil screening ,the re-moistened soil samples were incubated overnight for at least 12 h before being measured. However, since the initial emission deflection caused by remoistening decreased again after this time, the remoistening had no influence on the measured values.

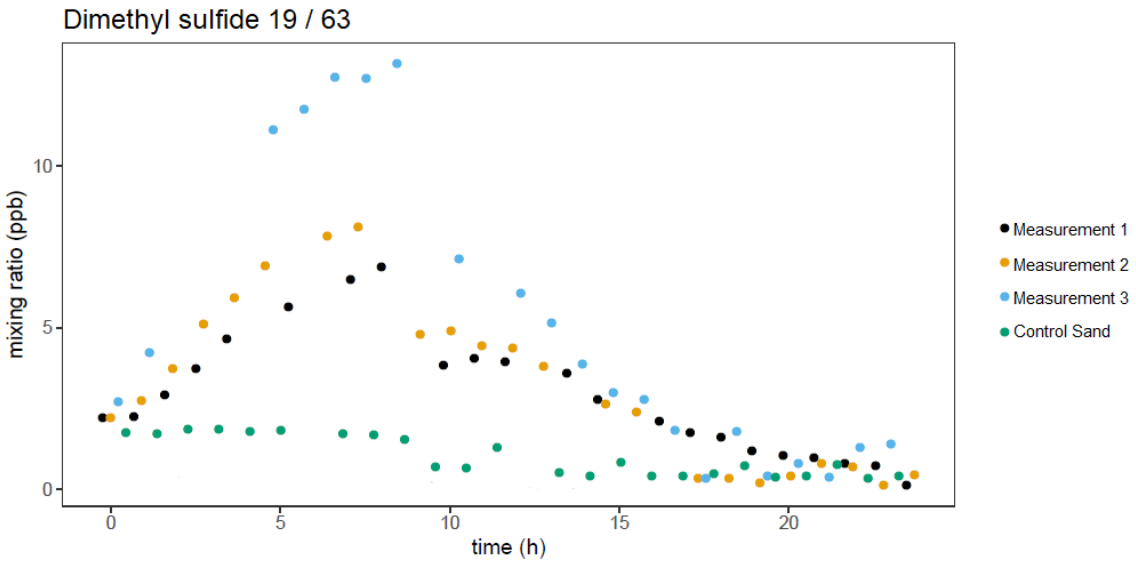

Figure 17: Time curve of DMS emissions during anoxic incubation over 24 h. The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

4.2.3 Comparison of oxic and anoxic incubation conditions

To compare VOC emissions under anoxic and oxic conditions, two redox chambers were filled with soil. One was then fumigated with nitrogen and the other with VOC-free air. Figure 18 shows that DMS emissions increase steadily during anoxic incubation until they reach values of about 0.13 ppb.

The gas flow through the chambers was reduced from 500 ml/min to 300 ml/min after two days to increase the time for the dissolution of the VOCs in the gas phase and therefore increase the intensity of the measurement. These procedures had the desired effect of increasing the measurable VOC emissions, but also led to a jump in the course of the measurements (cf. 3.4.2 Comparison of oxic and anoxic conditions).

In addition, a drop in the measured values between 100 h and 120 h (4-5 days) can be seen. This could be caused by fluctuations of the N_2 gas flow of the house gas pipeline of the MPI Jena during the weekend. This assumption could be verified by checking two parallel measurements over the weekend, where the nitrogen is drawn once from the house pipeline and once from a separate gas tank.

The calculation is shown in chapter 3.4.2 Comparison of oxic and anoxic conditions. DMS shows no emissions during oxic incubation.

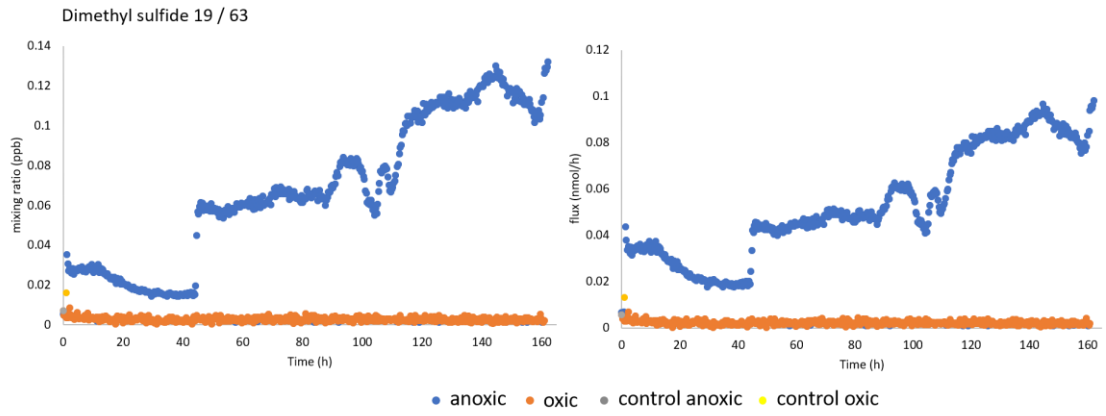

Figure 18: Course of DMS emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

With methanol 19/33, it's the other way around. It shows higher emissions with oxic incubation than with anoxic incubation. Thereby methanol emits at approx. 0.25 ppb under oxic- and at approx. 0.5 ppb under anoxic conditions. The values neither increase nor decrease over time. Also, the lower values of the anoxic incubation remain relatively constant during the experiment. After about half of the time the emissions of the anoxic incubation increase strongly and then decrease again until the initial values are reached (cf. Figure 19). This sudden change in the course can also be observed in the curves of pyruvic acid, acetone and propanal (cf. A3 Comparison of oxic and anoxic incubation Figure 43-Figure 45). Since this change in the emission values, as in the case of DMS, occurs during the period of 100 h to 120 h (4-5 days), this could also be due to a flow fluctuation in the gas flow of the Institute's pipeline.

In contrast to the course of the DMS emissions, the application of the flow against time causes a jump in the measured values instead of reducing it. One explanation for this would be that no methanol emissions could be measured at all and that the data is background noise from the device. This assumption is supported by the fact that the two control values measured at the beginning are at the same level as the remaining measured values.

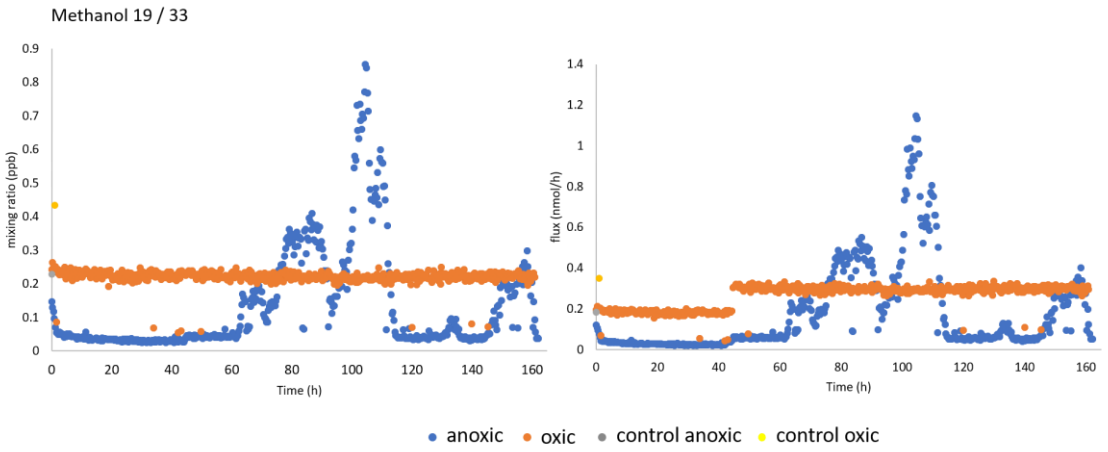

Figure 19: Course of methanol emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

The emissions of methanethiol 19/49 are shown in Figure 20 and display higher values for anoxic incubation than for oxic incubation. At the beginning of the experiment, the values of both conditions remain relatively constant. However, the emissions of the anoxic incubation increase towards the end from about 0.02 ppb to about 0.025 ppb.

The jump which results from the representation of the flow against time could be due to the fact that the relatively constant initial values of the measurement (0-110 h), similar to the methanol data, are background noise and only towards the end of the experiment real emissions became detectable. This assumption is confirmed by the fact that the initially measured control values are at the same level as the measured values between 0 h and 110 h and that the measured values only increase above the control values afterwards.

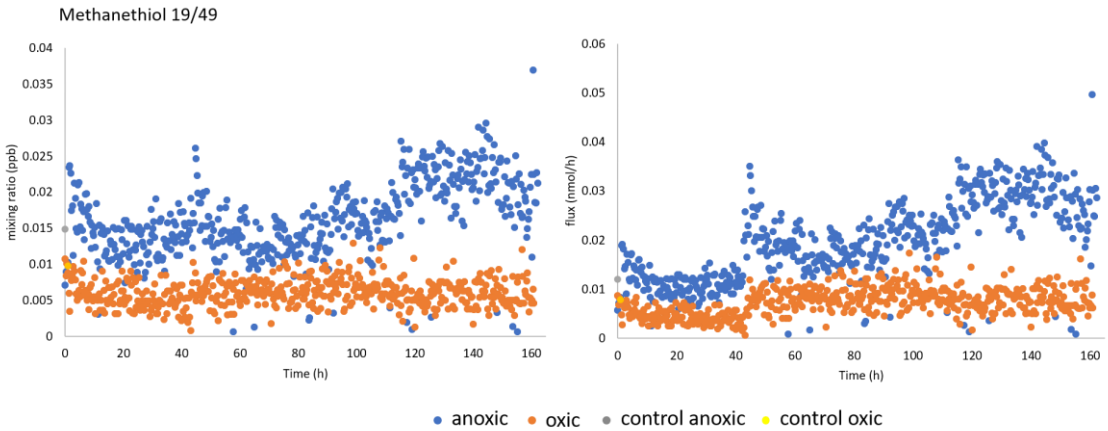

Figure 20: Course of methanethiol emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

The anoxic and oxic incubation of pyruvic acid 19/43, acetone 32/43 and propanal 30/57 show no differences in intensity. Pyruvic acid emits under both conditions at a

constant level of about 0.3 ppb (cf. Figure 43). The emission values of acetone are at approx. 0.4 ppb during the whole period and the emissions of propanal at approx. 0.6 ppb (cf. A3 Comparison of oxic and anoxic incubation Figure 44 and Figure 45). All three processes are interrupted in half of the experiment by a sudden increase in the anoxic emission values. The representation of the flow versus time generates a jump in all emission curves which leads to an increase in the emission values of both curves.

Just as with methanol before, the measured values of the control samples are at the same level, if not higher, than the measured values of the samples. Therefore, it can be assumed that this is the background signal and that the soil shows no significant emissions of pyruvic acid, acetone and propanal during the experiment. This assumption is supported by the fact that, as before, these measurements will jump if the flow is plotted against time. In addition, no relevant emissions could be measured for formic acid and hydrogen sulfide.

In summary, DMS 19/63 and methanethiol 19/49 are the only two substances that showed emissions in comparison with the substances previously determined in other experiments (cf. 4.2.1 Soil screening, 4.3.1 Drying experiment and 4.3.2 Oxygen free incubation experiment). DMS with maximum values of about 0.14 ppb shows higher values than methanethiol with 0.03 ppb. Both substances emit only with anoxic incubation, whereby the DMS emission values already rise after a time of approx. 80 h (ca. 3 days) and methane ethanol shows an increase in emissions after 110 h (ca. 4.5 days).

The redox potential measurements shown in Figure 21 and Figure 22 display a decrease of the redox potential from approx. 500 mV to approx. 350 mV during anoxic incubation. In contrast to the data from other experiments (4.3.1 Drying experiment), the measured values of different electrodes marginally differ from each other. With oxic incubation, an increase in the redox potential from approx. 400 mV to 450-500 mV can be observed for some electrodes (electrodes 6 and 7). The values of other electrodes (electrodes 8 and 2) remain relatively. This shows that with anoxic incubation the redox values are much lower than under oxic conditions and the values increase or decrease within the first 16 h and then remain relatively constant during the rest of the experiment. The curves of the anoxic data (chamber 2) are slightly broader than those of the oxic incubation data (chamber 3). This means that the measured values of one electrode vary more. In oxic incubation, on the other hand, the values of one electrode fluctuate less, making the differences between the individual electrodes more visible. These dif-

ferences could indicate individual subregions in the soil which are slightly more anoxic than others despite oxidic incubation.

The different variation of the measured values of one electrode in both chambers indicates technical differences and probably has nothing to do with the type of incubation (oxic/anoxic). This is confirmed by the redox curves in chapter 4.3.1 Drying experiment, where both chambers (chamber 2 and 3) were incubated anoxically. The stronger variation of the measured values in chamber 2 suggests that the respective electrode measures less accurately than in chamber 3, which is probably due to technical reasons.

If one compares the redox data with the emission curves of DMS 19/63 and methanethiol 19/49 during anoxic incubation, it can be seen that the redox values have already decreased and are relatively constant at approx. 300-400 mV, while the emissions do not show up until a later point. This can be explained by the delay in the release of the metabolites produced by the microorganisms. They change the metabolism as soon as an anoxic milieu has formed but the diffusion of the released substances takes a certain time, depending on the layer thickness and water content of the soil. In addition, the substance molecules are stopped on their way by adhesion effects on soil surfaces. Furthermore, the microorganisms need a certain amount of time to produce as many metabolites as they need to exceed the limit of detection of the SIFT-MS device. As already shown in the chapter 4.2.1 Soil screening, the water content has an influence on the quantity of measured VOCs, as a lot of water inhibits the diffusion of the substances. This could be a further explanation for the fact that the emissions of DMS and methanethiol only increase after 3 days and 4.5 days, as the soil in the chambers has already dried slightly during this time period.

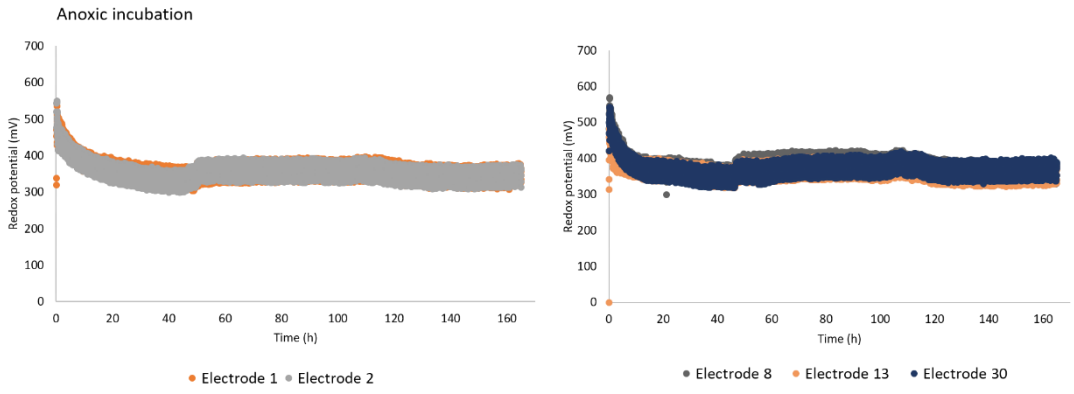

Figure 21: Redox potential courses of different electrodes during anoxic (N_2) incubation of the soil samples. Soil: SB II 10-20 cm site “M”, gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

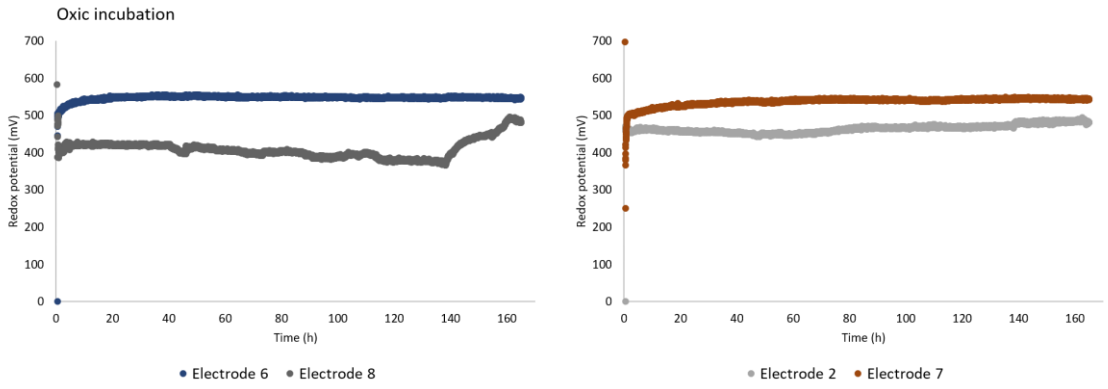

Figure 22: Redox potential courses of different electrodes during oxic (VOC free air) incubation of the soil samples. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

4.3 Main experiments

Finally, the two main experiments were planned and carried out with the help of the knowledge gained previously. This was done to answer the hypotheses previously made. Which is the assumption that the VOC emissions and the redox potential of the soil samples behave differently under anoxic and oxic incubation conditions. In addition, it was assumed that the changing soil moisture during the drying experiment also influences these parameters.

4.3.1 Drying experiment

In order to determine how the redox potential and the VOC emissions behave with decreasing water content under anoxic conditions, the soil samples were dried under N_2 gas flow in the redox chambers.

The SIFT-MS measurements show an increase in DMS 19/63, methanol and methanethiol emissions over the course of the drying experiment. It is noticeable that the emissions decrease again towards the end of the experiment after reaching a maximum. This maximum was approx. 0.8 ppb for DMS in experiment A and could not be reached in experiment B, since the curve still rises with no visible turning point (cf. Figure 23).

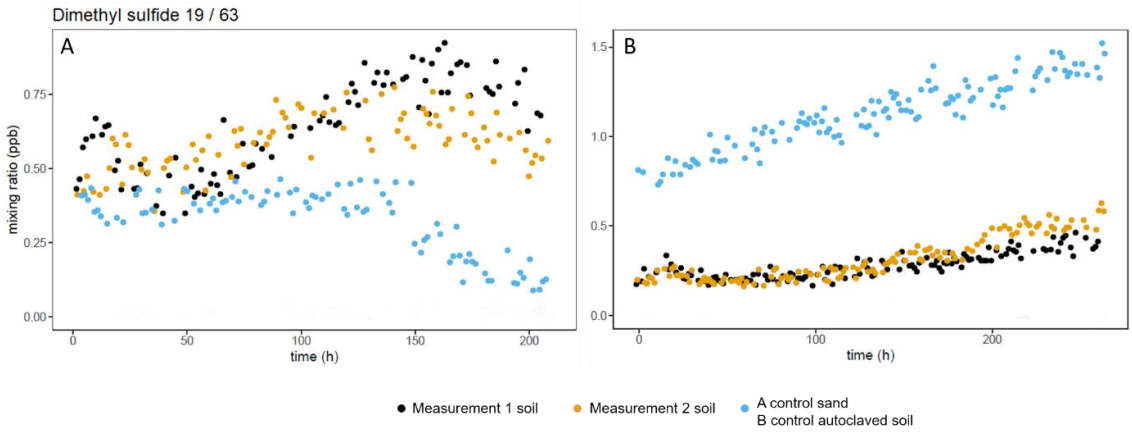

Figure 23: Time course of the DMS emissions of the two drying experiments (A and B) over the drying period. N_2 Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

The course of methanol 30/62 emissions also shows a turning point in Experiment A in contrast to Experiment B. They reach maximum values of about 200 ppb. However, the two measurement curves of Experiment A differ, since the first one reaches very high values, whereas the second one also increases, but only up to a value of approx. 50 ppb (cf. Figure 24).

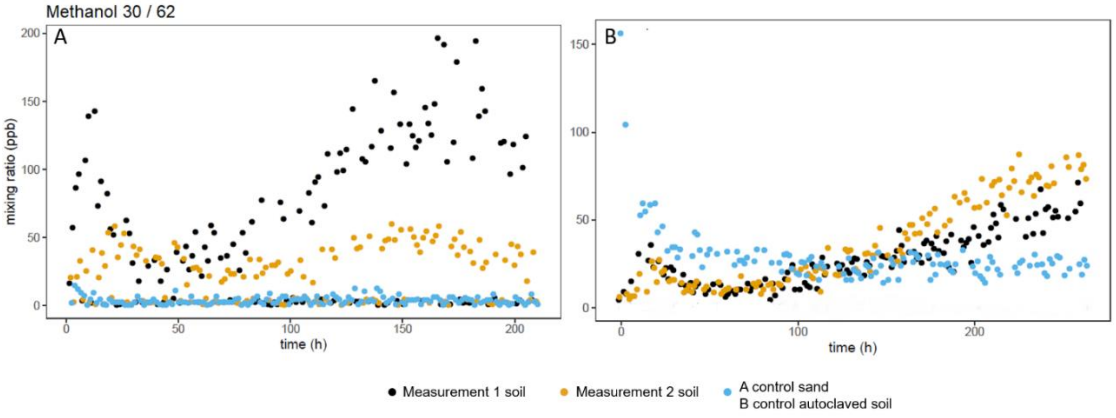

Figure 24: Time course of the methanol emissions of the two drying experiments (A and B) over the drying period. N_2 Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

The methanethiol emissions of both experiments reach similar maximum values of 0.9 ppb during the experimental run. In the curve of experiment A is no turning point whereas in experiment B a decrease of the methanethiol emissions can be observed (cf. Figure 25).

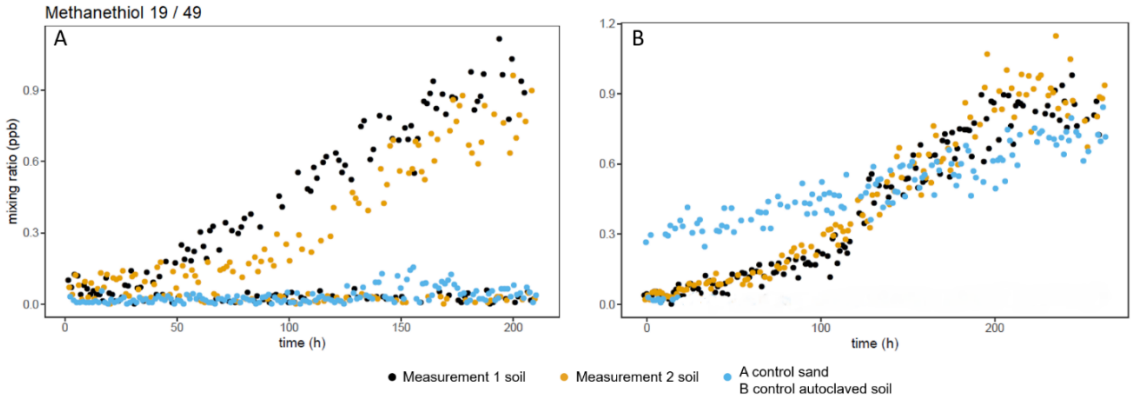

Figure 25: Time course of the methanethiol emissions of the two drying experiments (A and B) over the drying period. N_2 Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

Both SIFT-MS measurements of acetone and propanal show no emissions in Experiment B. In experiment A, acetone shows an increase in both measurements compared to the sand control. However, the two curves behave differently, since measurement 1 rises much faster and steeper than measurement 2. Measurement 1 already reaches values of up to approx. 100 ppb at half the time, with measurement 2 reaching maximum values of approx. 70 ppb only towards the end of the measurement. The values of propanal in experiment A lie between 2-5 ppb, but do not exceed the emissions of the sand control (cf. A4 Drying experiments Figure 48). Formic acid and pyruvic acid could be detected only in Experiment A. Both measurements show emissions, but only measurement 1 is higher than the sand control. For formic acid it reaches values of approx. 4 ppb, up to approx. 6 ppb and pyruvic acid up to approx. 40 ppb (cf. A4 Drying experiments Figure 49and Figure 50). In contrast to previous experiments (cf. 4.3.2 Oxygen free incubation experiment), no emissions of formaldehydes or hydrogen sulfide were detected. The emission curves of measurements 1 and 2 of pyruvic acid and formic acid differ greatly from each other and are therefore difficult to compare (cf. A4 Drying experiments Figure 49 and Figure 50). As before, the autoclaved soil shows higher emissions than sand in direct comparison.

In summary it can be said that the previously described courses of the DMS 19/63 and methanol 30/62 emissions show a faster achievement of the emission peak in experiment A (cf. Figure 23 and Figure 24).

This could be due to the fact that with a similar weight of the soil samples only 15 ml of water were added to the samples of experiment A and 50 ml of water to the samples of experiment B. The emission peak in experiment A was reached much faster. A possible

reason for this is the higher water content of the samples from experiment B, which led to a delay in the diffusion of the VOCs, so that these could only be measured at a later point in time when the soil had a slightly lower water content. In addition, the gas flow of approx. 300 ml/min in experiment A compared to the gas flow of 200 ml/min in experiment B led to faster drying of the soil samples, which further reinforces this effect. Furthermore, it can be seen that the longer duration of experiment B cannot compensate these factors, since the emission peak is not reached.

In contrast to the DMS and methanol emissions, methanethiol 19/49 shows a different course, since the emission peak is reached in experiment B and is not visible in experiment A (cf. Figure 25).

In addition, it is noticeable that the control samples used (wet sand and autoclaved soil) are extremely different. The autoclaved soil shows considerably higher emissions than the sand control, which in some cases even exceed the measured values of the soil (cf. Figure 23 and Figure 25). This suggests that the method of autoclaving the soil three times by heat and pressure, results in the soil being poorly usable as a control sample. This could be because both, the chemical composition and the basic structure of the soil are altered by autoclaving. The high pressure and high temperatures could lead to reactions in the soil and changes in the structure could facilitate the release of volatile substances, which is characterised by higher VOC emissions during measurement. This assumption is supported by the fact that the soil smells strongly of caramelized sugar after autoclaving, which clearly indicates a change in the chemical composition. For future experiments another more gentle way of sterilization should be found.

If one compares the redox curves of different electrodes in Experiment A, both measurements show that the values of electrode 1 and 2 are very similar. First, there is an increase of the redox potential to approx. 600 mV after the start of the measurement. Subsequently it drops again during anoxic incubation and then remains constant in the range from 300 mV to 400 mV. However, there are also some electrodes whose measuring process is different. Electrodes 8, 13 and 30, for example, have very different to fluctuating curves, whereby the values of electrode 30 even reach low redox potential values of approx. 0 mV (cf. Figure 26 and Figure 27).

This leads to the conclusion that, as already assumed in 4.2.3 Comparison of oxic and anoxic incubation conditions, different closed reaction spaces exist in the soil, which are

differently anoxic or oxic. This could be partly due to the fact that the fumigation does not penetrate so deeply into the soil, especially at high soil moisture levels, in order to achieve the same conditions at all points. A further reason for this observation could be different microorganisms accumulating in the different reaction rooms, which differ in number and species and consume existing oxygen reservoirs at different speeds and synthesize different metabolites, which in turn have an effect on the redox potential. The lower soil moisture towards the end of the drying experiment also favours the release of volatile substances from the soil, which also influences the conditions in the soil and thus the redox potential.

As previously described in 4.2.3 Comparison of oxic and anoxic incubation conditions, the individual electrodes in chamber 2 (Experiment A) are affected by greater measurement fluctuations than those in chamber 3 (Experiment B).

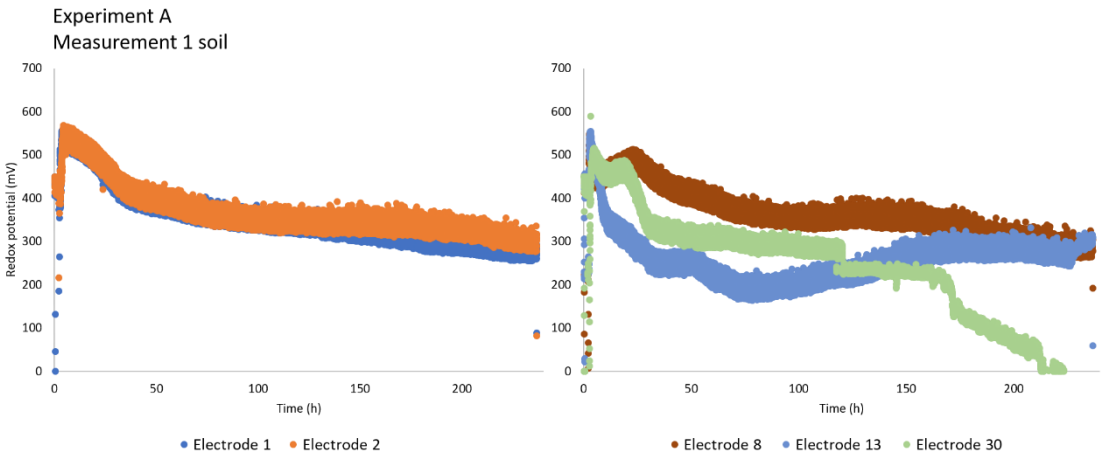

Figure 26: Redox potential of different electrodes during measurement of soil samples in measurement 1 of Experiment A. N_2 Gas flow: 300 ml/min, water added: 15 ml.

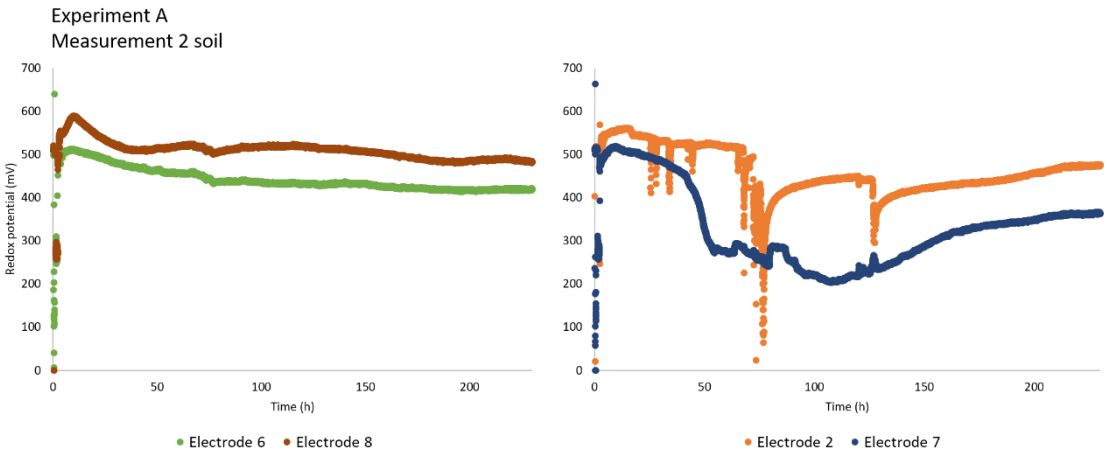

Figure 27: Redox potential of different electrodes during measurement of soil samples in measurement 2 of Experiment A. N_2 Gas flow: 300 ml/min, water added: 15 ml.

This observation is confirmed by Experiment B, as the various electrodes also have different redox potential curves. In measurement 1 the redox potential values of electrode 1 and electrode 2 decrease from 500-600 mV to 400-500 mV. Other electrodes (electrodes 13 and 30) even show a stronger decrease of the values up to 100 mV. The curves of electrode 6 & 8 are similar to those of electrode 1 and 2, as the values decrease over time from about 600 mV to 350-400 mV. Other electrodes (electrode 2 and 7) show stronger fluctuations during measurement 2. There, the redox potential drops partially to approx. 200-300 mV and -100 mV (cf. Figure 28 and Figure 29).

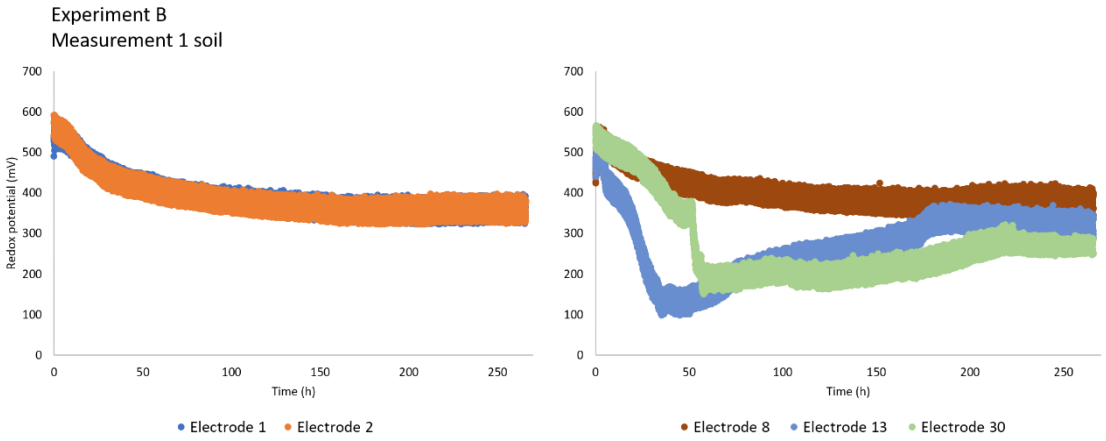

Figure 28: Redox potential of different electrodes during measurement of soil samples in measurement 1 of Experiment B. N_2 Gas flow: 200 ml/min, water added: 50 ml.

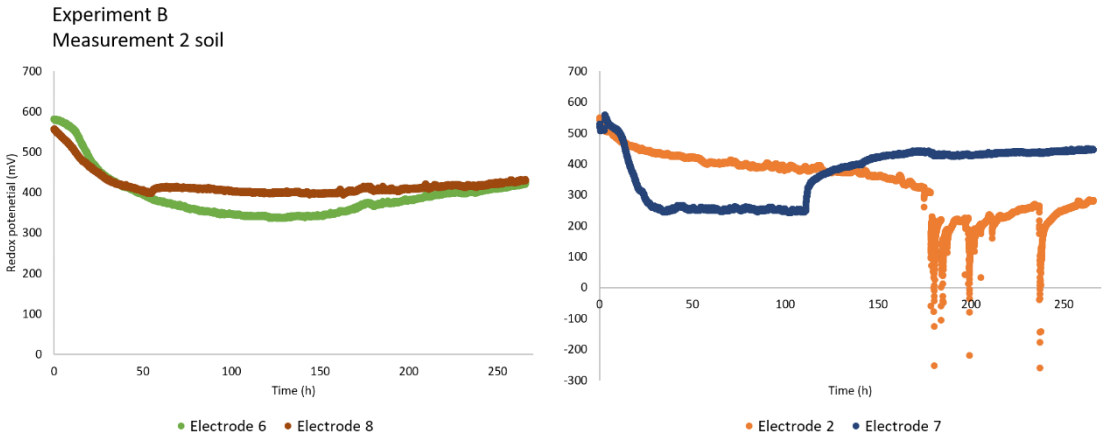

Figure 29: Redox potential of different electrodes during measurement of soil samples in measurement 2 of Experiment B. Gas flow: 200 ml/min, water added: 50 ml.

The sand control sample of experiment A shows strong fluctuations after the previously relatively constant values of electrodes 6, 15 and 17 break off after approx. 2 days. Towards the end of the experiment all measured values are between approx. 200 mV and 400 mV. Electrodes 6 and 17 of experiment B show a similar course. There the redox potential first increases and then decreases until both curves settle at approx. 200 mV.

As with the previous measurement of soil samples, the measurement of the autoclaved soil control also shows some electrodes with different courses. Thus, the curve of the electrode 15 initially deviates strongly from that of the other two, since the values drop to approx. -100 mV. Afterwards, the values increase again until the course of electrode 15 follows the course of the other electrodes (electrode 6 and 17) and level off at approx. 100 mV (cf. Figure 30).

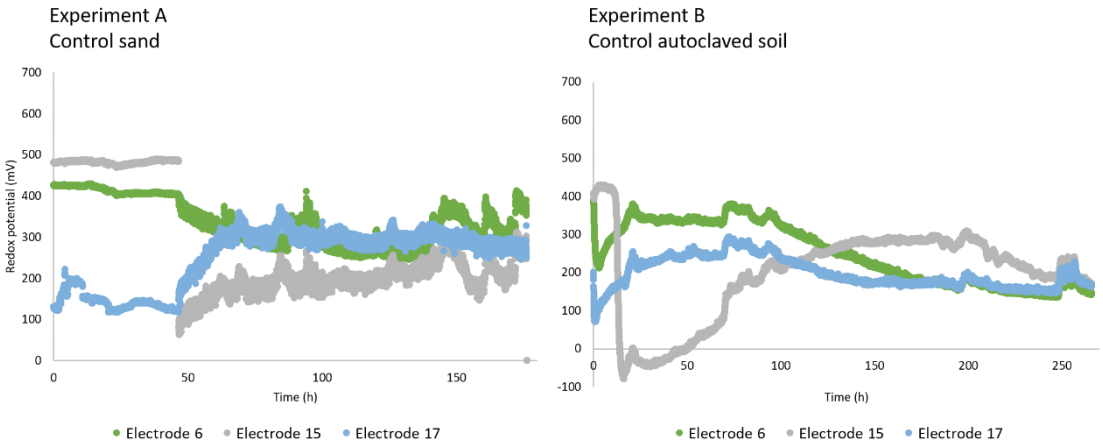

Figure 30: Redox potential of different electrodes during measurement of control samples in Experiment A and B. N_2 Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B).

If one compares the VOC emissions (cf. Figure 23-Figure 25) with the redox data, it can be seen that the VOC emissions from DMS, methanol and methanethiol only increase significantly after 100-200 h (4-8 days), although the redox values had already decreased considerably by then. As already mentioned in 4.2.3 Comparison of oxic and anoxic incubation conditions, the delay of the microbial metabolism in combination with the easier diffusion at lower water content of the soil samples could be responsible for this. Although the redox values in the experiments (A and B) decrease equally quickly, the two experiments differ in the speed of the increase in VOC emissions.

In addition, the graph of DMS emissions indicates that the soil was almost dry after about 150 h, resulting in fewer water molecules in the gas phase above (cf. Figure 23). This has an effect on the spectrum as the measured concentration in the SIFT-MS depends on the ratio product ion intensity/ reagent ion intensity. The reagent ions quickly decrease in humid air, which leads to higher concentration measurements. The turning point in the graph is therefore a sign of the drying of the soil sample, as the concentration decreases, which cannot be a pure biological effect.

4.3.2 Oxygen free incubation experiment

The oxygen free incubation experiment was carried out in 250 ml Schott bottles over a period of five weeks in order to verify the assumption that the emissions differ after anoxic incubation of different lengths and that a course over time as well as a change in the redox potential and the elemental composition can be seen.

This assumption is based on the fact that the redox potential decreases during anoxic incubation because oxygen is an electron donor with a high redox potential whose absence alters the redox potential in the soil. In addition, this behaviour of the redox potential during anoxic incubation has already been confirmed in previous experiments (cf. 4.2.3 Comparison of oxic and anoxic incubation conditions). The emissions and elementary composition should therefore also change over a longer period of time, since the soil microorganisms must return to other electron donors for energy production. This causes substances in the soil with higher redox potential to be metabolized to ones with lower E_N, leading to emissions of the more volatile substances, a change in chemical composition in the soil and again leads to a decrease in E_N.

Figure 31 shows that DMS emissions increase continuously over four weeks during anoxic incubation. The emissions increase from approx. 0.07 ppb from the beginning to approx. 1 ppb after week 4. methanol also shows a continuous increase from about 1 ppb at the start to about 3 ppb at the end of the four weeks. Both the values of dimethyl sulfide emissions and methanol emissions are higher than those of sand control. The values of the autoclaved soil are considerably higher.

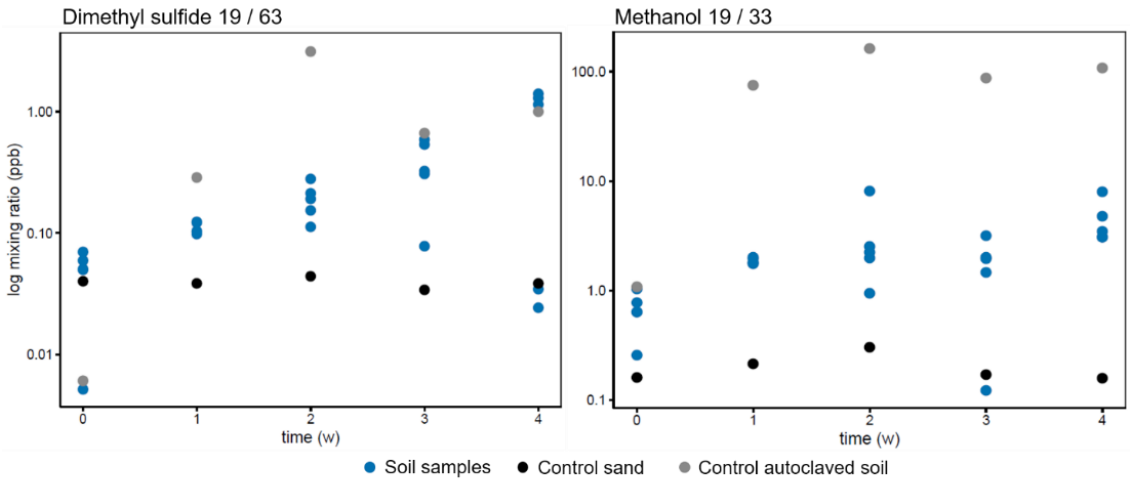

Figure 31: Time course of dimethyl sulfide (left) and methanol (right) emissions over 4 weeks.

The emissions of acetone and propanal behave similarly over the period of anoxic incubation but differ greatly in their intensity. The values for acetone rise from approx. 10 ppb to approx. 20 ppb by week two, but then drop slightly again. Propanal emissions start at values of approx. 0.3 ppb and reach approx. 0.6 ppb in week two. Then they decrease in week three but reach approx. 0.6 ppb again at the end of the experiment. All measured values are above the sand control (cf. Figure 32).

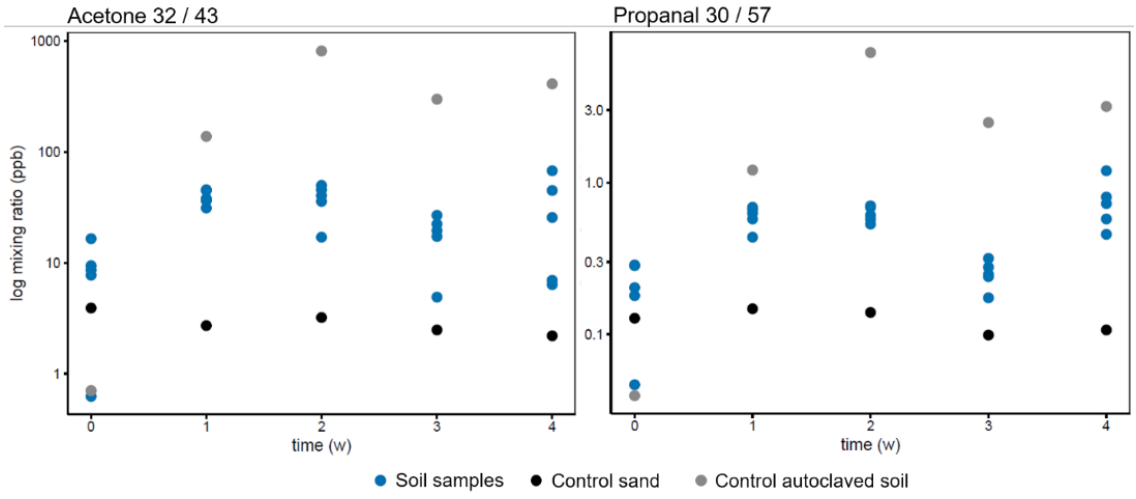

Figure 32: Time course of acetone (left) and propanal (right) emissions over 4 weeks.

Figure 33 shows an increase in formaldehyde emissions from about 1 ppb to about 3 ppb within the four-week incubation period. Formic acid starts at higher values of approx. 10 ppb at the beginning over approx. 30 ppb in week one. Subsequently, the emissions decrease again to up to approx. 3 ppb at the end of the experiment. The values of the sand control are below all measured values. The values of the autoclaved soil are similarly low at the beginning but rise above the values of the substance measurements after one week.

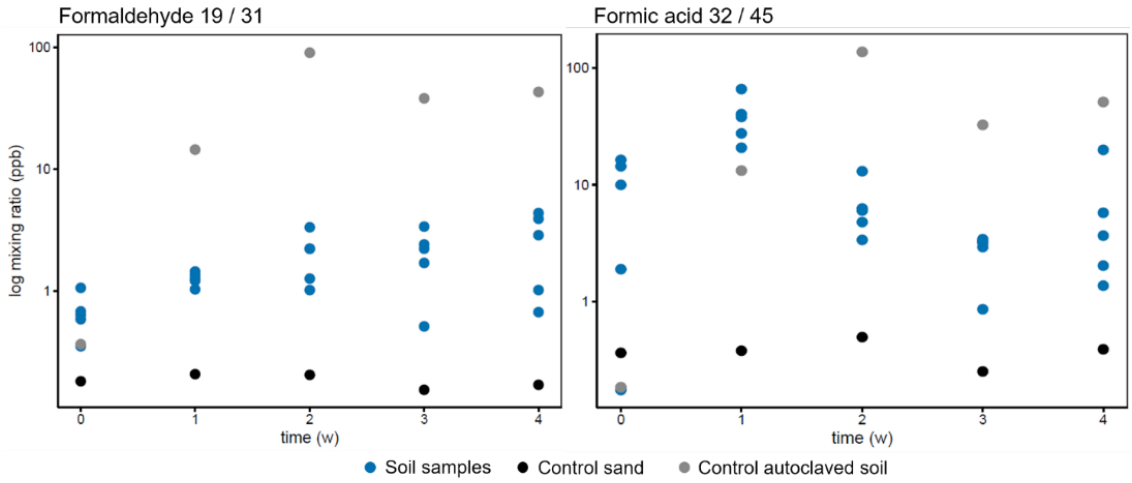

Figure 33: Time course of formaldehyde (left) and formic acid (right) emissions over 4 weeks.

Both the hydrogensulfide emissions and the methanethiol emissions increase continuously over the period of incubation. The hydrogenlsulfide values start at approx. 0.1 ppb and reach approx. 3.0 ppb in week four. Methanethiol emissions are lower and start between 0.01 ppb and 0.03 ppb. Within the next weeks they then rise to approx. 0.3 ppb. The sand control in both measurements is below the emissions of the soil samples. The emissions of the autoclaved soil are higher for hydrogen sulfide than for the soil samples. In the case of methane ethanol, however, these are below the measured values, but still higher than the measured values of the sand control (cf. Figure 34).

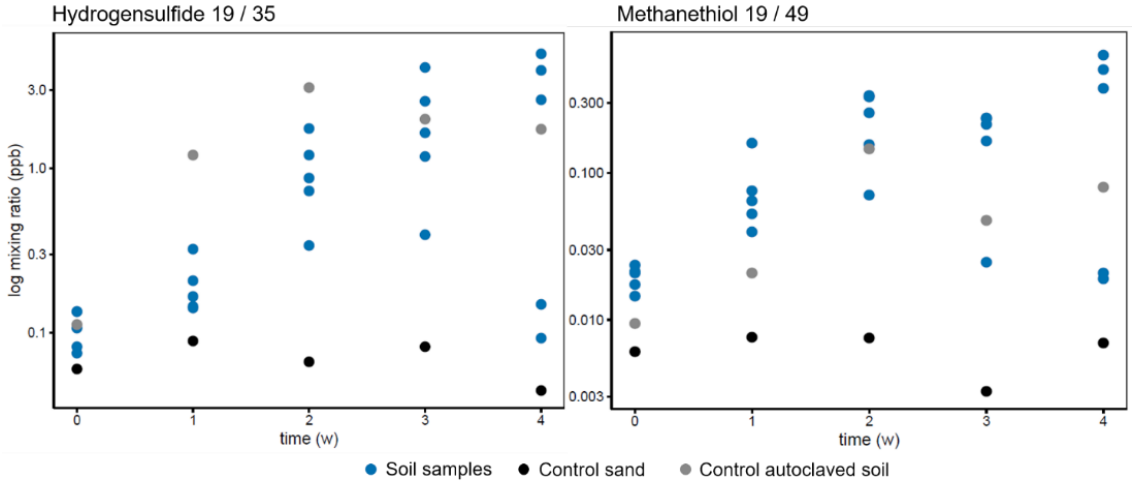

Figure 34: Time course of hydrogensulfide (left) and methanethiol (right) emissions over 4 weeks.

The emission pattern of pyruvic acid increases towards the middle of the experiment and then decreases again. Pyruvic acid shows emissions of approx. 30 ppb in week one, which then rise to 190 ppb and then fall slightly again. The emissions of most soil sam-

ples are above those of the sand control and below those of the autoclaved soil (cf. Figure 35).

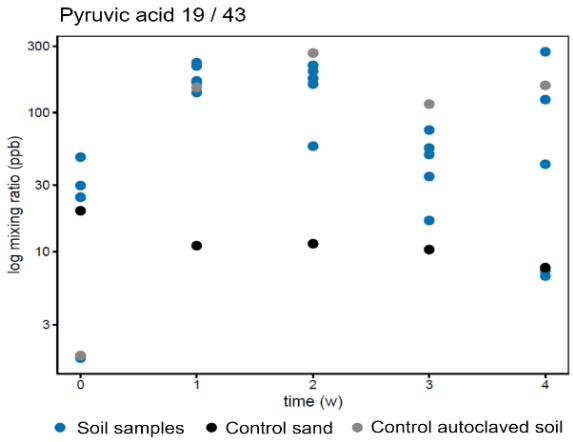

Figure 35: Time course of pyruvic acid emissions over 4 weeks.

As already mentioned earlier (cf. 4.3.1 Drying experiment), the measured values of the autoclaved earth often exceed those of the remaining samples. This is most likely caused by the change in soil structure and chemical composition of the soil during the autoclaving process. As a result, this type of sterilization is poorly suited for inactivating the microorganisms in the control sample and other ways should be found.

It is surprising that the substances which emit best in this experiment, such as Acetone 32/43 (about 50 ppb), Formic acid 32/45 (about 70 ppb) and Pyruvic acid 19/43 (about 200 ppb), are the substances which could hardly or not at all be measured during the other experiments (cf.4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment). In addition, it was found out that in contrast to the other experiments also formaldehyde 19/31 and hydrogen sulfide 19/35 emissions were found. (cf. Figure 31-Figure 35).

This could be due to the fact that these substances are produced in very low concentrations over long periods of time. Due to the continuous gas flow of the two previous experiments they were quickly transported away and were too low to generate meaningful signals. Due to the incubation in the airtight sealed bottles, these substances could accumulate and therefore be measured in higher concentrations. In addition, the oxygen free incubation experiment was started for four weeks while the 4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment experiments were finished after about two weeks.

If one compares the DMS emissions with each other, it can be seen that after approx. 160 h they were about 0.14 ppb in experiment (cf. 4.2.3 Comparison of oxic and anoxic incubation conditions, Figure 18) and about 0.75 ppb in experiment (4.3.1 Drying experiment, Figure 23), while after a four week incubation in the bottles a concentration of about 1 ppb DMS was reached. It must be taken into account that in the other two experiments the water content of the sample decreased over the incubation period, whereas it remained the same in the bottles.

Methanol 30/62 emissions in the two previous experiments (4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment) were approximately 0.03 ppb and around 150 ppb after 150 h incubation. This already represents a big difference, which can be explained by the complexity of the soil samples. Since these samples may contain different microorganisms, groups and conditions which may favour or hinder the production of certain metabolites. In the bottles the concentration of methanol after four weeks of anoxic incubation was about 10 ppb which is between the other two emission values. The fact that the second measurement of the 4.3.1 Drying experiment of methanol does not reach 150 ppb but is considerably lower (approx. 50 ppb) also supports this explanation.

Furthermore, Methanethiol 19/49 shows maximum values in the 4.2.3 Comparison of oxic and anoxic incubation conditions experiment after approx. 140 h at 0.03 ppb and in the 4.3.1 Drying experiment after approx. 200 h at 0.9 ppb. The emission values of methanethiol after four weeks of anoxic incubation in the bottles are about 0.3 ppb which is between the values of the previous experiments.

The measurement results of one chamber of the redox potential determination of the second week are shown in Figure 36. No clear change in the redox potential can be observed when the soil is applied to the electrodes, as the measured values are all very different and vary greatly. The other redox data of the different time points are also not representative.

The values that could be recorded with the portable redox probe from week 4 onwards are between 329-375 mV_H in week three and 331-346 mV_H in week four (cf. Table 10). Between the two weeks no decrease or increase of the redox values can be observed. Since the measurements of the first weeks are missing, however, the redox values are probably already settled. As far as the level of the measured values is concerned, they

are in the same range between 300-400 mV as those of the experiment 4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment. This suggests that similar substance emissions can also be observed here based on the results of these two experiments.

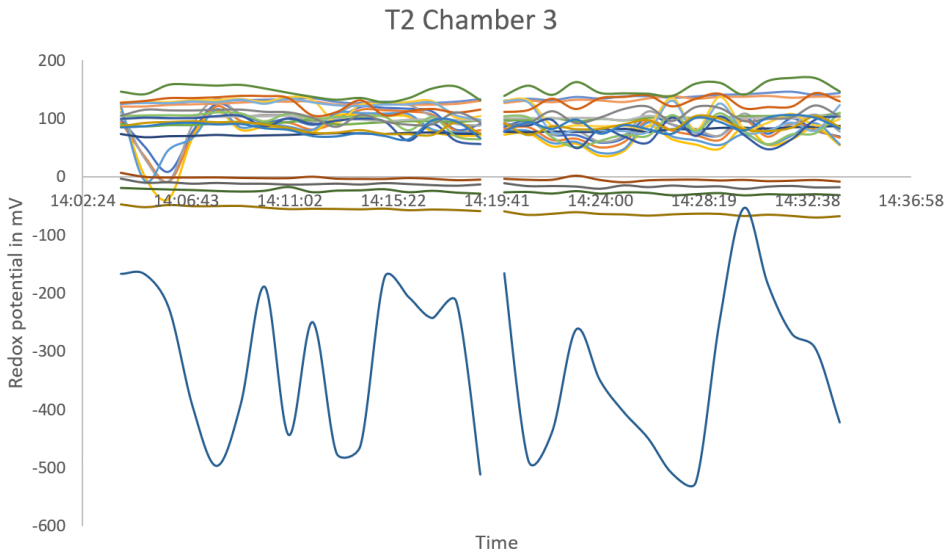

Figure 36: Redox data of different electrodes in chamber 3 after week 2.

The values of the gas analysis are shown in Table 10 in chapter A5 Oxygen free incubation experiment. If you compare them graphically, you can see that the CO_2 concentration increases over the incubation period of four weeks in the headspace of the bottles. Especially between the last two weeks a strong increase from approx. 8000 ppm to approx. 24000 ppm can be observed (cf. Figure 37). The curve of CH_4 behaves in a similar way, but in comparison to the CO_2 values only a maximum of approx. 700-800 ppm could be measured (cf. Figure 38).

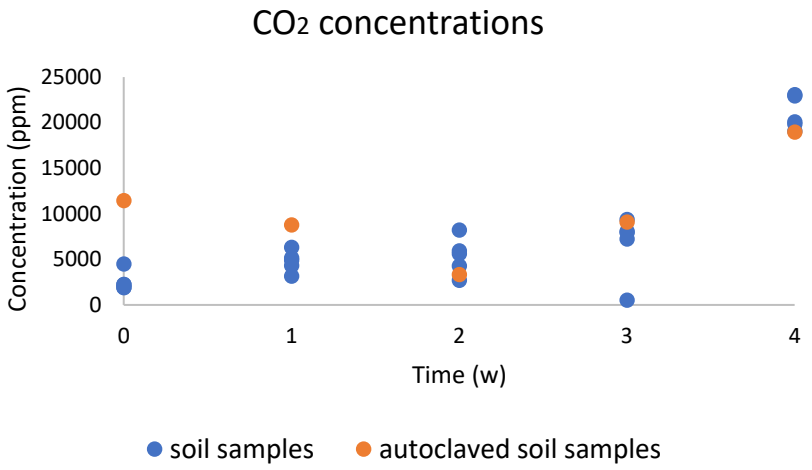

Figure 37: Course of Headspace CO_2 concentration in the different bottles during the four-week incubation period. Wet soil weight: ca. 120 g per bottle, Water added: 100 ml.

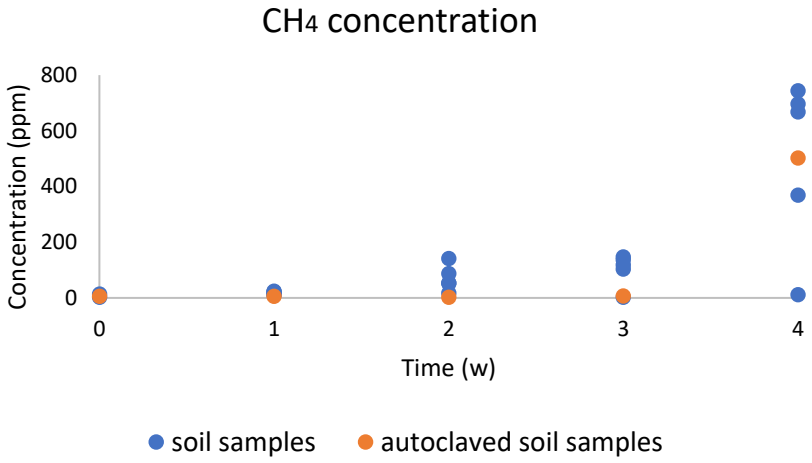

Figure 38: Course of Headspace CH_4 concentration in the different bottles during the four-week incubation period. Wet soil weight: ca. 120 g per bottle, Water added: 100 ml.

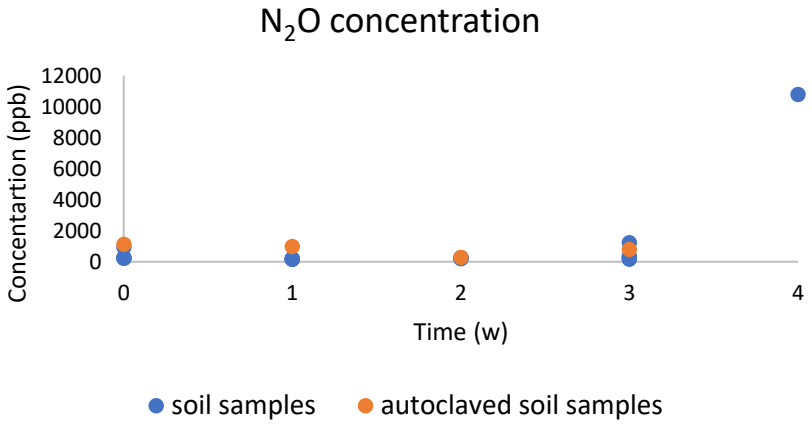

Figure 39: Course of Headspace NO_2 concentration in the different bottles during the four-week incubation period. Wet soil weight: ca. 120 g per bottle, Water added: 100 ml.

In contrast to CO_2 and CH_4, N_2O could only be detected in the ppb range. Here, as well, one can see a slight increase over time, whereby in week 4 only a particularly high value of one sample could be measured while the others were not detectable. Here the concentrations range between approx. 200-1000 ppb (cf. Figure 39).

The photometrically determined nitrite contents are shown in A5 Oxygen free incubation experiment in Table 10. They show that the nitrite values of the first two measurements (week 0 and 1) were below the detection limit (approx. 3 µg/l) of the device and from week 2 until the end of the incubation they are constant between 4 µg/l and 9 µg/l.

In summary, the results in this chapter show that the VOC emissions of all substances described above (DMS, Methanol, Acetone, Propanal, Formaldehyde, Formic acid, Hydrogensulfide, Methanethiol and Pyruvic acid) increase in the course of the anoxic incubation. In particular, acetone, formic acid and pyruvic acid showed high emissions at a redox potential of approx. 300-400 mV, which had already been measured in previous experiments with anoxic incubation. The increase over the incubation period is also evident in the gas analysis and the concentrations of CO_2, CH_4 and NO_2 obtained from this. The photometrically determined nitrite content also shows an increase from week 1 to week 2 but remains relatively constant between 4 µg/l and 9 µg/l just like the redox potential.

Due to a malfunction of the analytical instrument, it was not possible to determine the elementary composition, the nitrate/ nitrite content as well as the sulphate content of the SB II 10-20 cm site "M" soil samples as planned (cf. 3.2.2 Nitrate /Nitrite extraction, 3.2.3 Sulphate extraction and 3.2.4 Elementary analysis).

5 Evaluation and discussion

The following chapter clarifies the extent to which the hypotheses previously made could be confirmed. In addition, the relationships and conclusions from the results are discussed and compared with existing studies in order to obtain an overall picture of the processes in the investigated soil. First the influences of different parameters on the used analysis methods are discussed in order to evaluate optimal conditions for subsequent experiments. Subsequently, it will be determined how different conditions in the soil affect the measurement of VOC emissions and redox potential and whether the assumptions previously made relate to them. In the discussion of the two main experiments it will then be clarified to what extent the two main hypotheses relate and which conclusions can be drawn from them and in comparison, with existing studies.

5.1 Method development

First, the extent to which the assumptions regarding the effects of the internal chamber pressure and the gas flow apply to the measurement of emissions using SIFT-MS will be determined.

5.1.1 Pressure experiment

The hypothesis that the internal chamber pressure has an effect on the quantity of measured VOC emissions could be disproved for the pressure range between 1 bar and 3 bar. At first, it was assumed that a higher internal chamber pressure would lead to a higher resistance for the dissolution of the VOCs in the gas phase, which would lead to less VOC emissions.[86]

As the DMS measurements of three replicas at each of the three different pressures in the order 1 bar, 2 bar and 3 bar (replica 1-3) and then 3 bar 2 bar 1 bar (replica 4-6) show, the values decrease in the order of the measurements (cf. Figure 8).

This leads to the conclusion that smaller pressure differences of 1-2 bar, contrary to the previous assumption, can be well compensated by the installed overflow and have barely any effect on the measurement results.

The consequence for subsequent experiments is that the gas pressure in the range between 1 bar and 3 bar can be freely selected, as this does not change the measurement results, provided an overflow is installed. However, if experiments with larger pressure differences should be carried out, the extent to which the overflow can compensate this should be tested before.

5.1.2 Gas flow experiment

The hypothesis that the gas flow through the chamber as well as the flow into the SIFT-MS device has an influence on the amount of measured gas emissions could be confirmed. This hypothesis is based on the fact that due to a higher gas flow through the chamber, the VOCs have less time for the solution in the gas phase, as this is removed faster. A higher flow into the SIFT-MS, on the other hand, ensures that more substances enter the device and can be measured.

Moist sand was used instead of soil samples for the measurement and water emissions were investigated. This was because these emissions are constant in contrast to the VOC emissions, since they are not influenced by the metabolism of the microorganisms, only by the equilibrium between gas phase and soil.

The measurements at different ratios between the gas flows through the chamber and those into the SIFT-MS device showed that the last one has a greater influence on the amount of water measured. The highest Emissions could be measured at a gas flow of approx. 100 ccm into the SIFT-MS and approx. 110-150 ccm through the chambers (cf. Figure 9). since the gas flow through the chambers should always be higher than that into the SIFT-MS device, higher flows into the device automatically result in higher flows through the chambers. As the gas flow through the chambers cannot be selected too high due to the pressure increase and the faster drying of the soil samples, the experiments 4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment were performed at a chamber flow rate of approx. 300 ccm and 200 ccm.

5.1.3 Flow fluctuation experiment

It was assumed that measurement failures observed in previous experiments were caused by fluctuations in the gas flow. To check this assumption, two gas flow control units (GCU and MFC) were tested and the DMS emissions were measured using SIFT-MS. Since the measured values did not indicate any measurement failures due to flow fluctuations, the initial hypothesis for the failure was rejected.

On closer inspection of the data of the erroneous measurements, it became apparent that these were always 0. This confirmed the conclusion that the measured value errors could not be caused by flow fluctuations. The complete absence of a measured value subsequently led to the assumption that the sample did not get into the instrument in the first place. In consultation with SIFT-MS experts, the SIFT-MS inlet was finally identified as the most likely source of error (cf. 3.2.6 SIFT-MS measurement). Accordingly, the switching between the different ports does not always work during longer measure-

ments of different samples. If such an error occurs, the port remains closed and the gas flow does not enter the instrument, which means that no emissions can be measured. Since the problem could not be solved during this work, the failed measurements were removed from the graphs for evaluation.

5.2 Preliminary experiments

5.2.1 Soil screening

The following chapter covers the hypothesis that the VOC emissions of the Schlöppnerbrunnen soil samples differ according to iron content, water content and soil depth. This hypothesis could be confirmed and the details are discussed in the following.

The measurements of the VOC emissions of the soil samples showed emissions of DMS, acetone, propanal, methanol, formic acid and pyruvic acid. The highest emissions can be observed with the bond samples of the site "M" and a water content of 30 % and/ or 60 % WHC. Only DMS differs from the other substances as it shows the highest emission values (approx. 0.075 ppb) for the soil sample SB II 0-10 cm site "C".

One reason why DMS emissions could be measured is that, according to other studies, DMS can be produced via different biosynthetic pathways. Thus, both oxic and anoxic production of the substance is possible. Since the experiment was carried out under VOC free air flow, i.e. under oxic conditions, it is very likely that DMS was synthesized from metionin by methylation of methanethiol (MeSH). This is possible due to a gene called "*Mdda*", which codes for a methyltransferase. This gene occours in different groups of bacteria such as sediment dwelling *Pseudomonas sp.*, nitrogen-fixing *Bradyrhizobia sp.* as well as myco- and cyanobacteria. Especially in the meta-genome of soil bacteria, the gene is present in 76 % of bacteria.[87]

The acetone measured in this experiment is mainly known as a fermentation product of different clostridia strains in which it is formed by the enzymatic decarboxylation of acetoacetic acid. Preliminary studies also suggest the possibility of acetone production by methylobacteria such as *Methylosinus trichosporium* from poly-/L hydroxybutyric acid (PHB) via 3-hydroxybutyrate and acetoacetate.[88]

Methanol occurs very frequently in soil emissions, since it is synthesized mainly by fermentation of cellulose from decaying plant material.[89]

Organic acids such as formic acid and pyruvic acid, whose emissions could be measured in this experiment, are produced during the inorganic solution of phosphates by various

soil microorganisms such as *Pseudomonas sp*. This makes the phosphates in the soil more accessible and thus supports plant growth.[90,91]

One explanation why more VOC emissions could be measured in the Fe richer soil of the site "M" is that many bacteria including facultatively anaerobic soil bacteria are using a ferric reductase system for energy production from the reduction of iron substances.[92]

In addition, other studies on the iron content of the Schlöppnerbrunnen fen have shown Fe(III)-reducing and Fe(II)-oxidizing bacteria coexisting across all depths. The increased iron content serves as an electron transport system for energy production in various microorganism groups under oxic and anoxic conditions.[75]

This energy production of the microorganisms in the more ferrous Schlöppnerbrunnen site "M" ensures that the microorganisms multiply faster and their metabolic processes are increased. This likely results in higher emissions of VOCs compared to site "C".

Besides the iron content, it also turned out that the water content had an influence on the amount of measured emissions. This is because higher soil moisture levels promote the growth of microorganisms and support anoxic metabolic processes, but at the same time inhibit the diffusion of VOCs. Since the highest emissions could be measured mainly at 30-60 % WHC, the diffusion seems to have a greater influence on the emission of VOCs.

For further experiments these results indicated that the soil samples SB II 10-20 cm site "M" are most suitable as the influences of different parameters on the VOC emissions can be better recognized due to the high VOC emissions. It was also hypothesized that in experiments where the water content changes over time, the decrease can be related to an increase in detectable VOCs (cf. 3.4.2 Comparison of oxic and anoxic conditions and 3.5.1 Drying experiment).

5.2.2 Incubation time experiment

The assumption that the incubation period and remoistening of the soil had an effect on the measurement results of the 4.2.1 Soil screening experiment, could not be confirmed. The DMS 19/63 emissions over 24 h show an increase of the emissions immediately after the humidification of the soil. The maximum of the emission peak is reached after approx. 8-10 h before the measured values drop again and after approx. 15 h reached their initial values. This shows that remoistening within the first 12 h leads to an initial increase in VOC emissions and that incubation time differences between several samples have an influence on the results during this period (cf. Figure 17).

However, this fact did not affect the 4.2.1 Soil screening experiment, as the samples were incubated for about 16 h after remoistening and the initial peak of the VOC emissions has already decreased after this time.

For all future rewetting experiments, it should be noted that the samples should be incubated sufficiently in advance to prevent falsification of the measurement results by the rewetting peak.

5.2.3 Comparison of oxic and anoxic incubation conditions

For this experiment, the hypothesis that VOC emissions and redox potential values behave differently under anoxic and oxic incubation conditions was confirmed and are discussed in the following.

In contrast to 5.2.1 Soil screening only emissions of DMS and methanethiol were found, but these differed greatly from each other depending on the anoxic or oxic incubation. DMS 19/63 was emitted during anoxic incubation, whereas no emissions were observed during oxic incubation. After approx. 100 h fumigation with N_2, the previously relatively constant DMS emission values began to rise and reached a maximum of approx. 0.14 ppb after approx. 150 h. At the same time, this maximum represented a turning point, as the emissions dropped again until the end of the experiment. No emissions of DMS 19/63 could be seen during oxic incubation (cf. Figure 18). The emissions of methanethiol 19/49 showed the same behaviour, reaching maximum values of approx. 0.03 ppb at an incubation time of 150 h (cf. Figure 20).

As expected, the redox values of the anoxic incubation also differed from those of the oxic incubation. Thus, they decreased from approx. 400 mV to 300-400 mV within the first 20 h after the beginning of the anoxic incubation and remained constant at this level during the remaining time. The redox values of the oxic incubation increased from 400 mV to 400-500 mV immediately after the start of the experiment and also remained constant for the rest of the time. Differences in the redox values were found in the curves of different electrodes (cf. Figure 21 and Figure 22).

If the two values are brought into a context, it shows VOC emissions of DMS and methane ethanol can be observed at redox potential values between 300-400 mV but are not emitting at higher redox values of 400-500 mV.

As already described under 5.2.1 Soil screening, DMS can be synthesized under both oxic and anoxic conditions.[87] The results of this experiment show only emissions during anoxic incubation, suggesting that DMS in this case is synthesized by methylation of methanethiol.[93]

Methanethiol in turn can be synthesized by microorganisms from sulfur-containing amino acids such as methionine.[94]

This relationship between DMS and methanethiol explains why their processes are so similar. Because after an increase in methane ethanol production, DMS production increases since it is synthesized from methanethiol.

In other studies where the influence of oxic and anoxic conditions should be investigated, similar values were found as in this thesis. Thus, the redox potential fell rapidly from approx. 600 mV to 200 mV due to a rapid change from incubation under oxygen impact to argon gassing. This behaviour could also be observed in this work, even if only minimum values of approx. 300 mV could be achieved. According to the other study, this is due to the length of the previous oxic incubation, since the decrease of the redox potential at O_2 exclusion lasts longer after longer incubation under O_2 influence. Since the soil samples of this experiment were not taken and stored under exclusion of oxygen, this could be the reason for the weaker decrease of the redox values.[95,67]

Other work has already established a link between VOC emissions and certain redox potential values. However, the studies focus mainly on NO_2^- and methane emissions. They found that high NO_2^- emissions can be measured at redox potentials of approx. 250 mV. In contrast, methane emissions can only be measured at very low redox potentials of min. -150 mV and lower.[68,67] There is not much research about the connection between other VOC emissions and the redox potential. Therefore, no further comparison with other sources could be discussed here.

If one compares the time curves of the redox potential and the VOC emissions, one sees a delayed emission of DMS and methanethiol after the redox potential has already settled at approx. 300 mV (cf. Figure 18,Figure 20 and Figure 21). This is the case, because the diffusion of the metabolites takes time even with higher water contents. In addition, the substance molecules are stopped on their way by adhesion effects on soil surfaces. Furthermore, the microorganisms need a certain amount of time to produce as many metabolites as they need to exceed the limit of detection of the SIFT-MS device. In this experiment this time is about 130 h. As mentioned above, this delay of the emissions could be caused by the long storage of the soil samples under oxic conditions.[95]

For future experiments it can be concluded that an anoxic incubation of the soil samples is more suitable to investigate VOC emissions and that there is a direct relationship between the emissions and the redox potential in the soil. This relationship could also be used to increase the production of different metabolites by manipulating the redox po-

tential.[67] In addition, soil samples should not be exposed to too much oxygen to reduce the incubation time under gas flow and to see results faster.

5.3 Main experiments

The two main experiments served to establish a relationship between VOC emissions and redox potential and to investigate the effects of factors like water content, continuous gas flow or incubation in a closed system. In the following, the results of these experiments will be discussed in order to gain insights into the chemical and ecological relationships within the soil samples.

5.3.1 Drying experiment

The hypothesis that VOC emissions change over time during anoxic incubation under continuous gas flow was confirmed. Furthermore, as previously assumed, the water content had an influence on the emission of the substances. The assumption that VOC emissions are related to the measured redox potential is also true.

In Experiment A the wet soil samples were incubated for 200 h at a gas flow of approx. 300 ml/min and flooded with 15 ml water. Experiment B incubated for 250 h at a gas flow of about 200 ml/min. However, 50 ml water was added for flooding (cf. 3.5.1 Drying experiment).

The results of the VOC emission measurements of both experiments show emissions of DMS 19/63, Methanol 30/62 and Methanethiol 19/49. In both experiments, the DMS emissions rise steadily over the incubation period and reach their maximum in experiment A after approx. 150 h. The VOC emissions of the two experiments are measured in the same way. Subsequently, the emissions fall again until the end of the incubation period. In experiment B, no turning point is reached, since the DMS emissions rise to max. 0.5 ppb by the end. Methanol shows, depending on the experiment, the same course as DMS and reaches in experiment A a maximum of 200 ppb at the turning point. In experiment B the maximum values towards the end of the experiment are about 100 ppb. The methanethiol emissions also increase over the incubation time and reach in experiment A max. 0.9 ppb and in experiment B approx. 1 ppb. In comparison, the autoclaved soil sample from experiment B always shows higher emissions than the sand control in experiment A, whereby these even partially exceed the values of the other measurements (cf. Figure 23-Figure 25).

As already described above (cf. 5.2.1 Soil screening), DMS emissions are present under anoxic conditions due to the methylation of methanethiol, which in turn is synthesized

by soil microorganisms from sulfur-containing amino acids (e.g. Met), released by the degradation of organic material.[93,94]

Methanol, in turn, is a fermentation product, which can be produced by the anaerobic energy production of microorganisms from sugars. In the soil, sugar is produced from the degradation of cellulose from rotting plants.[89]

One reason why a turning point was seen in experiment A in a shorter period of time than in experiment B could be the higher water content in experiment B with a similar weight of the soil samples in both experiments. The higher soil moisture made the diffusion of VOCs more difficult and ensured that fewer emissions could be measured. In addition, the higher gas flow in experiment A leads to a faster drying of the soil samples. Since the emission values are determined by the ratio between production intensity and reagent intensity and a higher air humidity leads to a decrease in the reagent ions, higher air humidity can lead to higher emission concentrations. The turning point of the DMS and methanol emission in experiment A after approx. 150 h is therefore an indication that the soil samples are nearly dried out. Furthermore, it can be seen that the longer duration of experiment B cannot compensate these factors, since the emission peak is not reached (cf. Figure 23 and Figure 24).[96]

The results of the redox data show, that the redox potential values in experiment A drop from approx. 500-600 mV after approx. 50 h after the start of incubation to values between 300-400 mV (cf. Figure 26 and Figure 27). The data from experiment B show the same course (cf. Figure 28 and Figure 29). In both cases, individual electrodes show different values from this curve and, for example, sink much more strongly to up to 100 mV or 0 mV. This behaviour could already be observed in Experiment 4.2.3 Comparison of oxic and anoxic incubation conditions. The differences between individual electrodes could be caused, for instance, by different conditions in closed reaction chambers of the floor.

The two control samples (sand Experiment A and autoclaved soil Experiment B) show strong fluctuations of the redox potential values, so that no trend could be detected during incubation (cf. Figure 30).

If the VOC emission data are brought into connection with the redox potential measurements, the conclusions from the experiment can be confirmed. Since during this experiment a delay of the VOC emissions can be observed in comparison to the equilibration of the redox potential at about 300 mV. As discussed above, this can probably be

traced back to the diffusion barrier caused by high soil moisture, adhesion effects in the soil and overcoming the detection limit of the SIFT-MS device.

Since the measured redox values are directly related and caused by the chemical composition of the soil, conclusions can be drawn about the expected VOC emissions and vice versa.

Positive redox potential values of 200-300 mV, as measured in this experiment, indicate O_2 reduction and denitrification processes. The emissions of methane ethanol and DMS are indicators of sulfate reduction, which occurs only at lower redox potentials. Some electrodes were also able to record lower redox potential values, which suggests that more anoxic substructures exist in the soil in which the measured DMS and methanethiol emissions are produced. Methanol as a fermentation product is also produced only at very low redox potential values, which supports this assumption.[97,98]

These conclusions can be applied to future experiments. For example, the soil should be flooded so that it does not dry out too quickly during the experiment and no time remains for the adjustment of the redox potential and the production of VOCs by microorganisms. Too much water hinders the diffusion of the VOCs and leads to an unnecessary lengthening of the experiment until usable measured values are generated. Furthermore, it can be seen that the incubation time of 200 h for the set water content is not sufficient for the complete drying of the soil samples, which is why the incubation time should be extended for further experiments in order to observe the complete course of the VOC emissions and the redox potential during drying. Another important discovery gained from the experiment is that the suspected closed reaction spaces have a large influence on the production of certain VOCs, which in turn supports the hypothesis that the change in soil structure during autoclaving is one reason why it does not seem suitable as a control.

5.3.2 Oxygen free incubation experiment

The hypothesis that VOC emissions are related to the redox potential was confirmed. Furthermore, the assumption that VOC emissions during anoxic incubation in hermetically sealed bottles increase over a period of four weeks was confirmed.

Therefore, six soil samples including the autoclaved soil control were measured by SIFT-MS every week.

In addition, a gas analysis of the headspace was carried out and the redox potential was measured.

The SIFT-MS measurements showed emissions of DMS 19/63, Methanol 19/33, Acetone 32/43, Propanal 30/57, Formaldehyde 19/31, Formic acid 32/45, Hydrogensulfide 19/35, Methanethiol 19/49 and Pyruvic acid 19/43. All these substances showed an increase in emissions over the incubation period of four weeks. Acetone with max. 50 ppb, Formic acid with max. 70 ppb and Pyruvic acid with max. 200 ppb showed the strongest emissions (cf. Figure 31-Figure 35). If one compares these results with previous experiments, it becomes apparent that most of the substances could not be measured with anoxic incubation under continuous gas flow and drying out over time but could be measured in comparatively high concentrations in this experiment. This could be due to the fact that these substances are formed in lower concentrations over time and accumulate in the sealed bottles. In the case of continuous gas flow, these substances are removed too quickly so that they do not exceed the detection limit of the SIFT-MS device.

Why and under which conditions DMS, methanethiol, methanol, acetone and organic acids such as formic acid and pyruvic acid are formed in soil has already been discussed in the evaluation of previous experiments (cf. 5.2.1 Soil screening, 5.2.3 Comparison of oxic and anoxic incubation conditions and 5.3.1 Drying experiment). Formaldehyde and hydrogen sulfide could only be measured during this experiment and the 4.2.1 Soil screening experiment. That is why their formation is discussed in the following.

In earlier studies it became obvious that there is a formaldehyde cycle in biological systems. On the one hand, formaldehyde can be formed from S-adenosyl-L-methionine by various enzymatic transmethylation reactions. On the other hand, formaldehydes can be used for the methylation of L-methionines. It is also known that both formaldehydes and a demethylated substance can be formed during demethylation processes.[99]

Furthermore, it is known from previous studies that hydrogen sulfide, like DMS, can be formed via methanethiol starting with the amino acid methionine by soil microorganisms.[100]

If one compares the emission growth of the different substances with each other, it is noticeable that some increase at earlier times of incubation than others (cf. Figure 31-Figure 35).

In earlier studies, it was found that microorganisms initially use oxygen as an electron donor for energy production. If this is not available, the next most suitable electron donor is used, which leads to a change in the redox potential over time.[101]

If one applies this knowledge to the comparison of emission curves, a ranking is obtained in which the individual substances are formed under anoxic conditions. Thus, the

sulfate reduction takes place first, which leads to the formation of methanethiol. This is then used for the production of hydrogen sulfide and DMS. If the redox potential decreases even further methanogenesis and fermentation then take place, as a result, which leads to organic acids such as pyruvic and formic acid, as well as methanol formation.[53]

This is also evident in the curves of the gas emissions. The emission of methanethiol increases already in week two and decreases afterwards in week three while maximum emissions of DMS and hydrogen sulfide only occur in the last week (cf. Figure 31 and Figure 34). In addition, one sees the maximum emissions of the fermentation product methanol only during the last measurements of the experiment (cf. Figure 31).

The redox values measured with the portable electrode for week three and four show values between 300-400 mV like discovered in previous experiments (cf.4.2.3 Comparison of oxic and anoxic incubation conditions and 4.3.1 Drying experiment). In order to obtain further information about the redox potential during the four weeks, the results of the gas analytical measurement of CH_4 and the photometric determination of the nitrite content can be used. In earlier studies, these were often associated with certain redox potential values and can therefore be used for indirect estimation.[102]

The gas analysis of CH_4 showed an increase in emissions over a period of four weeks. The increase in CH_4 concentration from week three to week four from approx. 200 ppm to 800 ppm was particularly high (cf. Figure 38). As mentioned earlier, CH_4 production is a sign of very low redox potential (-200 mV).[69] This indicates the existence of very anoxic sub-regions in the soil, as such low redox potentials could not be measured with the large redox electrode. On the other hand, it confirms the previously discussed differences in course, which indicate the use of sulfate reduction and fermentation towards the end of the experiment and thus low redox potentials. The formation of nitrite is also an indicator for low redox potentials. This assumption is supported by the fact that the nitrite concentration of the soil samples was below the detection limit until week two but increased to 5-9 µg/l in week three and remained in this range until the end of the experiment (cf. Table 10).

From these results it can be assumed that there is a direct correlation between redox potential and VOC emissions. The complexity of the chemical processes in the soil is also illustrated by the fact that gas emissions are also related to each other. In addition, the presumed substructures and closed reaction spaces may have a great influence on the local production of certain substances, which is why the redox potential at different points in the soil can vary greatly. For further experiments it should not be assumed that

certain substances are not formed, because it is possible, that they could not be detected under continuous gas flow.

This could be due to the fact that the substances emit in lower concentrations over longer time periods. The measurement with the redox chambers better depicts the various redox potential distributions in the soil than a single large electrode. However, it is not suitable for single measurements because the sample came into contact with too much oxygen during application, which can quickly change the redox potential and falsify the results.

In conclusion, it can be said that the main hypothesis of this work regarding a direct relationship between VOC emissions and the redox potential could be confirmed.

6 Conclusion and outlook

The main aspect of this work was to establish a link between VOC emissions and redox potential. Two main experiments were performed on the anoxic incubation of the selected Schlöppnerbrunnen soil samples (SB II 10-20 cm site "M"). In previous studies it has already been shown that there is a relationship between CH_4 and NO_2^- emissions from soils with the redox potential. This work also dealt with other VOCs such as DMS, methanol, acetones, hydrogen sulfide, methanethiol, formaldehydes and organic acids. In the process, a correlation between VOC emissions and the redox potential could be established both for the drying out of the soil samples over a period of approx. two weeks under anoxic conditions and for the four-week anoxic incubation of the soil samples.

After a short delay due to diffusion and adhesion effects, the VOCs increased after the redox potential dropped. An additional finding that could be gained from the results of these experiments is the influence of the water content on the measurement of VOC emissions. Although higher soil moisture levels promote microbial growth, they also impede the diffusion of the VOCs produced. The redox chambers used contain many small electrodes, which are distributed throughout the soil and therefore well represents its complexity. Based on these results it could be assumed that small closed reaction rooms exist in the soil, which offer different conditions and have a strong influence on the production of VOCs and thus on the redox potential.

In order to continue and complete the investigations of this work, the integration of the elementary analysis data as well as the determined nitrite and sulphate contents of the investigated soil could be integrated into the context. A molecular biological investigation of the microbiome of the soil samples could provide additional information about the complex ecological relationships in the soil.

In summary, it can be said that by examining the soil samples for water content, VOC emissions and redox potential under oxic and anoxic conditions, a direct relationship between the observed VOC emissions and the redox potential could be established.

7 Sources

[1] P. B. Reich, A. W. Schoettle, H. F. Stroo, J. Troiano, R. G. Amundson, *Can. J. Bot.* **1985**, *63*, 2049.

[2] H. Aaltonen, J. Aalto, P. Kolari, M. Pihlatie, J. Pumpanen, M. Kulmala, E. Nikinmaa, T. Vesala, J. Bäck, *Plant Soil* **2013**, *369*, 241.

[3] H. Insam, M. S. A. Seewald, *Biol Fertil Soils* **2010**, *46*, 199.

[4] J. W. Leff, N. Fierer, *Soil Biology and Biochemistry* **2008**, *40*, 1629.

[5] H. Aaltonen, J. Pumpanen, M. Pihlatie, H. Hakola, H. Hellén, L. Kulmala, T. Vesala, J. Bäck, *Agricultural and Forest Meteorology* **2011**, *151*, 682.

[6] C. Warneke, T. Karl, H. Judmaier, A. Hansel, A. Jordan, W. Lindinger, P. J. Crutzen, *Global Biogeochem. Cycles* **1999**, *13*, 9.

[7] A. Bachy, M. Aubinet, C. Amelynck, N. Schoon, B. Bodson, C. Moureaux, P. Delaplace, A. de Ligne, B. Heinesch, *Atmospheric Environment* **2018**, *176*, 229.

[8] C. C. Cleveland, J. B. Yavitt, *Appl. Environ. Microbiol.* **1998**, *64*, 172.

[9] S. M. Owen, S. Clark, M. Pompe, K. T. Semple, *FEMS microbiology letters* **2007**, *268*, 34.

[10] M. Kramshøj, I. Vedel-Petersen, M. Schollert, Å. Rinnan, J. Nymand, H. Ro-Poulsen, R. Rinnan, *Nature Geosci* **2016**, *9*, 349.

[11] A. C. Nölscher, A. M. Yañez-Serrano, S. Wolff, A. C. de Araujo, J. V. Lavrič, J. Kesselmeier, J. Williams, *Nature communications* **2016**, *7*, 10383.

[12] B. M. Delory, P. Delaplace, M.-L. Fauconnier, P. Du Jardin, *Plant Soil* **2016**, *402*, 1.

[13] D. Asensio, J. Penuelas, R. Ogaya, J. Llusia, *Atmospheric Environment* **2007**, *41*, 2456.

[14] G. W. Schade, A. H. Goldstein, *J. Geophys. Res.* **2001**, *106*, 3111.

[15] K. S. Ramirez, C. L. Lauber, N. Fierer, *Biogeochemistry* **2010**, *99*, 97.

[16] S. H. Svendsen, A. Priemé, J. Voriskova, M. Kramshøj, M. Schostag, C. S. Jacobsen, R. Rinnan, *Soil Biology and Biochemistry* **2018**, *120*, 80.

[17] D. Asensio, S. Owen, J. Llusia, J. Penuelas, *Soil Biology and Biochemistry* **2008**, *40*, 2937.

[18] M. Mäki, J. Heinonsalo, H. Hellén, J. Bäck, *Biogeosciences* **2017**, *14*, 1055.

[19] W. K. Cornwell, J. H. C. Cornelissen, K. Amatangelo, E. Dorrepaal, V. T. Evin-er, O. Godoy, S. E. Hobbie, B. Hoorens, H. Kurokawa, N. Pérez-Harguindeguy et al., *Ecology letters* **2008**, *11*, 1065.

[20] Y. Kuzyakov, A. A. Larionova, *J. Plant Nutr. Soil Sci.* **2005**, *168*, 503.

[21] C. LIN, S. OWEN, J. PENUELAS, *Soil Biology and Biochemistry* **2007**, *39*, 951.

[22] J. Tang, G. Schurgers, R. Rinnan, *Rev. Geophys.* **2019**, *64*, 172.

[23] R. Rinnan, *Front. Microbio.* **2013**, *4*.

[24] C. M. Gray, R. K. Monson, N. Fierer, *J. Geophys. Res. Biogeosci.* **2014**, *119*, 547.

[25] P. Faubert, P. Tiiva, Å. Rinnan, S. Räty, J. K. Holopainen, T. Holopainen, R. Rinnan, *Atmospheric Environment* **2010**, *44*, 4432.

[26] S. Sawada, T. Totsuka, *Atmospheric Environment (1967)* **1986**, *20*, 821.

[27] C. M. Gray, R. K. Monson, N. Fierer, *J. Geophys. Res.* **2010**, *115*, 520.

[28] G. W. Schade, T. G. Custer, *Atmospheric Environment* **2004**, *38*, 6105.

[29] K. Jardine, A. M. Yañez-Serrano, J. Williams, N. Kunert, A. Jardine, T. Taylor, L. Abrell, P. Artaxo, A. Guenther, C. N. Hewitt et al., *Global Biogeochem. Cycles* **2015**, *29*, 19.

[30] Z. Yi, X. Wang, M. Ouyang, D. Zhang, G. Zhou, *J. Geophys. Res.* **2010**, *115*, 1052.

[31] http://wiki.biomine.skelleftea.se/wiki/images/thumb/5/51/Sulfur_cycle_flow_diagram.jpg/. 04.09.2019.

[32] M. O. Andreae, C. D. Jones, P. M. Cox, *Nature* **2005**, *435*, 1187.

[33] J. Stefels, M. Steinke, S. Turner, G. Malin, S. Belviso, *Biogeochemistry* **2007**, *83*, 245.

[34] I. Barnes, J. Hjorth, N. Mihalopoulos, *Chemical reviews* **2006**, *106*, 940.

[35] https://www.nationalgeographic.com/environment/global-warming/acid-rain/. 04.09.2019.

[36] J. B. Shukla, S. Sundar, et al. *Natural Resource Modeling* **2013**, *26*, 53.

[37] S. J. de Mora, R. Eschenbruch, S. J. Knowles, D. J. Spedding, *Food Microbiology* **1986**, *3*, 27.

[38] O. Carrión, J. Pratscher, A. R. J. Curson, B. T. Williams, W. G. Rostant, J. C. Murrell, J. D. Todd, *The ISME journal* **2017**, *11*, 2379.

[39] S. Corsetti, D. McGloin, J. Kiefer, *Fuel* **2016**, *166*, 488.

[40] H. Günzler, H.-U. Gremlich, *IR-Spektroskopie*. *Eine Einführung*, 4. Aufl., Wiley-VCH, Weinheim, **2012**.

[41] "Grundlagen der IR- und Raman-Spektroskopie - Chemgapedia", zu finden unter http://www.chemgapedia.de/vsengine/vlu/vsc/de/ch/3/anc/ir_spek/grundlagen.vlu.html. 12/12/2019.

[42] "DoITPoMS - TLP Library Raman Spectroscopy - Introduction", zu finden unter http://web.archive.org/web/20120511102714/http://www.doitpoms.ac.uk/tlplib/raman/intro.php. 12/12/2019.

[43] D. Cialla-May, M. Schmitt, J. Popp, *Physical Sciences Reviews* **2019**, *4*, 557.

[44] Petra.

[45] D. Materić, D. Bruhn, C. Turner, G. Morgan, N. Mason, V. Gauci, *Applications in plant sciences* **2015**, *3*.

[46] https://www.srainstruments.com/p/sift-ms/. 12/12/2019.

[47] D. Smith, P. Španěl, *Mass Spectrom. Rev.* **2005**, *24*, 661.

[48] C. Turner, P. Španěl, D. Smith, *Physiol. Meas.* **2006**, *27*, 321.

[49] www.syft.com/sift-ms/. 05.09.2019.

[50] https://www.syft.com/gc-ms-sift-ms-comparison/. 05.09.2019.

[51] A. Olivares, K. Dryahina, J. L. Navarro, D. Smith, P. Španěl, M. Flores, *J. Agric. Food Chem.* **2011**, *59*, 1931.

[52] https://www.internetchemie.info/chemie-lexikon/daten/e/elektrochemische-spannungsreihe.php. 12/12/2019.

[53] https://www.chemie.de/lexikon/Redoxpotential.html. 12/12/2019.

[54] B. Hölting, W. G. Coldewey, *Hydrogeologie. Einführung in die Allgemeine und Angewandte Hydrogeologie*, 8. Aufl., Spektrum Akademischer Verlag, Heidelberg, **2013**.

[55] R. Myrdal, *The Electrochemistry and Characteristics of Embeddable Reference Electrodes for Concrete*, Elsevier Science, Burlington, **2014**.

[56] B. Hölting, W. G. Coldewey, *Hydrogeologie. Einführung in die allgemeine und angewandte Hydrogeologie ; 90 Tabellen*, 7. Aufl., Spektrum Akad. Verl., Heidelberg, **2009**.

[57] A. R. Grable, E. G. Siemer, *Soil Science Society of America Journal* **1968**, *32*, 180.

[58] R. E. Farrell, G. D. W. Swerhone, C. van Kessel, *Communications in Soil Science and Plant Analysis* **2008**, *22*, 1059.

[59] J. Postgate, *Annual Reviews in Microbiology* **1959**, *13*, 505.

[60] R. D. Harter, E. O. McLean, *Agronomy Journal* **1965**, *57*, 583.

[61] W. E. Connell, W. H. Patrick, *Science (New York, N.Y.)* **1968**, *159*, 86.

[62] P. Vanysek, *CRC handbook of chemistry and physics* **2000**, *8*.

[63] D. E. Carter, *Environmental health perspectives* **1995**, *103 Suppl 1*, 17.

[64] H. L. Bohn, *Soil Science* **1971**, *112*, 39.

[65] A. X. Hou, G. X. Chen, Z. P. Wang, O. van Cleemput, W. H. Patrick, *Soil Science Society of America Journal* **2000**, *64*, 2180.

[66] Y. K., W. Z., V. A., W. P. Jr, O. van Cleemput, *Biol Fertil Soils* **2001**, *34*, 25.

[67] Z. P. Wang, R. D. DeLaune, W. H. Patrick, P. H. Masscheleyn, *Soil Science Society of America Journal* **1993**, *57*, 382.

[68] P. H. Masscheleyn, R. D. DeLaune, W. H. Patrick, *Chemosphere* **1993**, *26*, 251.

[69] K. Yu, S. P. Faulkner, W. H. Patrick, *Chemosphere* **2006**, *62*, 905.

[70] L. D. BAILEY, E. G. BEAUCHAMP, *Can. J. Soil. Sci.* **1973**, *53*, 213.

[71] M. Kralova, P. H. Masscheleyn, C. W. Lindau, W. H. Patrick, *Water Air Soil Pollut* **1992**, *61*, 37.

[72] P. Westermann, *Aquatic microbiology* **1993**, 215.

[73] O. Schmidt, M. A. Horn, S. Kolb, H. L. Drake, *Environmental microbiology* **2015**, *17*, 720.

[74] E. Gorham, *Ecological applications: a publication of the Ecological Society of America* **1991**, *1*, 182.

[75] S. Kügler, R. E. Cooper, C.-E. Wegner, J. F. Mohr, T. Wichard, K. Küsel, *The Science of the total environment* **2019**, *646*, 972.

[76] C. Estop-Aragonés, C. Blodau, *Soil Biology and Biochemistry* **2012**, *47*, 1.

[77] M. Reiche, A. Hädrich, G. Lischeid, K. Küsel, *J. Geophys. Res.* **2009**, *114*, n/a-n/a.

[78] J. P. Anderson, K. H. Domsch, *Canadian journal of microbiology* **1975**, *21*, 314.

[79] T. A. Pankratov, A. O. Ivanova, S. N. Dedysh, W. Liesack, *Environmental microbiology* **2011**, *13*, 1800.

[80] S. Schellenberger, S. Kolb, H. L. Drake, *Environmental microbiology* **2010**, *12*, 845.

[81] L. R. Lynd, P. J. Weimer, W. H. van Zyl, I. S. Pretorius, *Microbiology and molecular biology reviews: MMBR* **2002**, *66*, 506-77.

[82] M. Dworkin, S. Falkow, E. Rosenberg, K.-H. Schleifer, E. Stackebrandt (Hrsg.) *The Prokaryotes*. *Volume 2: Ecophysiology and Biochemistry*, Springer-Verlag, New York, NY, **2006**.

[83] I. Fung, J. John, J. Lerner, E. Matthews, M. Prather, L. P. Steele, P. J. Fraser, *J. Geophys. Res.* **1991**, *96*, 13033.

[84] R. Hein, P. J. Crutzen, M. Heimann, *Global Biogeochem. Cycles* **1997**, *11*, 43.

[85] A.-S. Lehnert, T. Behrendt, A. Ruecker, G. Pohnert, S. E. Trumbore, *Performance of SIFT-MS and PTR-MS in the measurement of volatile organic compounds at different humidities*, **2019**.

[86] http://www.3rd1000.com/chem101/chem103c.htm. 17/12/2019.

[87] O. Carrión, A. R. J. Curson, D. Kumaresan, Y. Fu, A. S. Lang, E. Mercadé, J. D. Todd, *Nature communications* **2015**, *6*, 6579.

[88] A. W. Thomson, J. G. O'Neill, J. F. Wilkinson, *Archives of microbiology* **1976**, *109*, 243.

[89] T. B. Johansson, H. C. Kelly, A. K. N. Reddy (Hrsg.) *Renewable energy*. *Sources for fuels and electricity*, Earthscan Publ, London, **1993**.

[90] P. Vyas, A. Gulati, *BMC microbiology* **2009**, *9*, 174.

[91] Y. Shen, L. Ström, J.-Å. Jönsson, G. Tyler, *Soil Biology and Biochemistry* **1996**, *28*, 1163.

[92] *Proceedings of Symposium on Paddy Soils*, 1. Aufl., Springer Berlin, Berlin, **2014**.

[93] E. G. Stets, M. E. Hines, R. P. Kiene, *FEMS Microbiology Ecology* **2004**, *47*, 1.

[94] R. P. Kiene, K. D. Malloy, B. F. Taylor, *Appl. Environ. Microbiol.* **1990**, *56*, 156.

[95] K. R. Reddy, W. H. Patrick, *Soil Biology and Biochemistry* **1975**, *7*, 87.

[96] L. W. Petersen, Y. H. El-Farhan, P. Moldrup, D. E. Rolston, T. Yamaguchi, *Journal of Environment Quality* **1996**, *25*, 1054.

[97] T. C. Stadtman, *Annual Reviews in Microbiology* **1967**, *21*, 121.

[98] *Advances in Agronomy*, Elsevier, **1968**.

[99] E. Tyihák, L. Albert, Z. I. Németh, G. Kátay, Z. Király-Véghely, B. Szende, *Acta biologica Hungarica* **1998**, *49*, 225.

[100] S. H. Zinder, T. D. Brock, *Appl. Environ. Microbiol.* **1978**, *35*, 344.

[101] C. Achtnich, F. Bak, R. Conrad, *Biol Fertil Soils* **1995**, *19*, 65.

[102] H. Flessa, F. Beese, *Soil Science Society of America Journal* **1995**, *59*, 1044.

Appendix

A1 SIFT-MS measurement

Table 6: Details of the SIFT-MS settings of the method testSoilDMS-s2-S11-long.sme with 11 measurement repetitions each.

Reagent m/z	Reagent	Product	Time limit in ms	Count limit	Comment
19	H_3O^+	18	500	10000	ammonia, NH_4^+
19	H_3O^+	19	500	10000	$H_3O^+(0)$
19	H_3O^+	31	500	10000	formaldehyde, CH_3O^+
19	H_3O^+	33	500	10000	methanol, CH_5O^+
19	H_3O^+	35	500	10000	hydrogen sulfide, H_3S^+
19	H_3O^+	36	500	10000	ammonia, $NH_4^+.H_2O$
19	H_3O^+	37	500	10000	$H_3O^+.H_2O$
19	H_3O^+	43	500	10000	pyruvic acid, $C_2H_3O^+$
19	H_3O^+	45	500	10000	acetaldehyde, $C_2H_5O^+$
19	H_3O^+	49	500	10000	methyl mercaptan, $CH_4S.H^+$
19	H_3O^+	49	500	10000	formaldehyde, $H_2CO.H^+.H_2O$
19	H_3O^+	51	500	10000	methanol, $CH_3OH_2^+.H_2O$
19	H_3O^+	53	500	10000	hydrogen sulfide, $H_3S^+.H_2O$
19	H_3O^+	55	500	10000	$H_3O^+.(H_2O)_2$
19	H_3O^+	59	500	10000	acetone, $C_3H_7O^+$
19	H_3O^+	59	500	10000	propanal, $C_3H_7O^+$
19	H_3O^+	61	500	10000	acetic acid, $CH_3COOH_2^+$
19	H_3O^+	63	500	10000	dimethyl sulfide,$(CH_3)_2S.H^+$
19	H_3O^+	63	500	10000	acetaldehyde, $C_2H_5O^+.H_2O$
19	H_3O^+	67	500	10000	methyl mercaptan, $CH_4S.H^+.H_2O$
19	H_3O^+	69	500	10000	methanol,

Reagent m/z	Reagent	Product	Time limit in ms	Count limit	Comment
					$CH_3OH.H^+.(H_2O)_2$
19	H_3O^+	73	500	10000	$H3O^+.(H_2O)_3$
19	H_3O^+	77	500	10000	ethyl methyl sulfide, $CH_3SHC_2H_5^+$
19	H_3O^+	77	500	10000	acetone, $(CH_3)_2CO.H^+.H_2O$
19	H_3O^+	77	500	10000	propanal, $C_3H_7O^+H_2O$
19	H_3O^+	79	500	10000	acetic acid, $CH_3COOH_2^+.H_2O$
19	H_3O^+	81	500	10000	acetaldehyde, $C_2H_5O^+.2H_2O$
19	H_3O^+	89	500	10000	butanoic acid, $C_3H_7COOH_2^+$
19	H_3O^+	91	500	10000	lactic acid, $CH_3CH(OH)COOH_2^+$
19	H_3O^+	95	500	10000	dimethyl disulfide, $(CH_3)_2S_2.H^+$
19	H_3O^+	95	500	10000	ethyl methyl sulfide, $CH_3SHC_2H_5^+.H_2O$
19	H_3O^+	95	500	10000	propanal, $C_3H_7O+._2H_2O$
19	H_3O^+	97	500	10000	acetic acid, $CH_3COOH_2^+.2H_2O$
19	H_3O^+	107	500	10000	butanoic acid, $C_3H_7COOH_2^+.H_2O$
19	H_3O^+	123	500	10000	benzoic acid, $C_7H_6O_2.H^+$
19	H_3O^+	137	500	10000	alpha-pinene, $C_{10}H_{17}^+$
19	H_3O^+	145	500	10000	octanoic acid, $C_8H_{16}O_2.H^+$
19	H_3O^+	159	500	10000	dimethyl tetrasulfide, $C_2H_6S_4^+$
19	H_3O^+	163	500	10000	octanoic acid, $C_8H_{16}O_2.H^+$
19	H_3O^+	177	500	10000	dimethyl tetrasulfide,

Reagent m/z	Reagent	Product	Time limit in ms	Count limit	Comment
					$C_2H_6S_4H^+.H_2O$
30	NO^+	30	500	10000	$NO^+(0)$
30	NO^+	43	500	10000	acetaldehyde, CH_3CO^+
30	NO^+	48	500	10000	$NO^+(1)$
30	NO^+	48	500	10000	$NO^+.(H_2O)1$
30	NO^+	57	500	10000	propanal, $C_3H_5O^+$
30	NO^+	61	500	10000	acetaldehyde, $CH_3CO^+.H_2O$
30	NO^+	62	500	10000	methanol, $NO^+.CH_3OH$
30	NO^+	71	500	10000	Butanoic acid, $C_3H_7CO^+$
30	NO^+	73	500	10000	lactic acid, $CH_3CH(OH)CO^+$
30	NO^+	78	500	10000	dimethyl sulfoxide, $C_2H_6OS^+$
30	NO^+	79	500	10000	acetaldehyde, $CH_3CO^+.2H_2O$
30	NO^+	88	500	10000	acetone, $NO^+.C_3H_6O$
30	NO^+	90	500	10000	acetic acid, $NO^+.CH_3COOH$
30	NO^+	94	500	10000	dimethyl disulfide, $(CH_3)_2S_2^+$
30	NO^+	104	500	10000	propanoic acid, $NO^+.C_2H_5COOH$
30	NO^+	108	500	10000	acetic acid, $NO^+.CH_3COOH.H_2O$
30	NO^+	118	500	10000	butanoic acid, $NO^+.C_3H_7COOH$
30	NO^+	118	500	10000	pyruvic acid, $C_3H_4O_3.NO^+$
30	NO^+	120	500	10000	lactic acid, $NO^+.CH_3CH(OH)COOH$
30	NO^+	124	500	10000	dimethylsulfone,

Reagent m/z	Reagent	Product	Time limit in ms	Count limit	Comment
					$C_2H_6O_2S.NO^+$
30	NO^+	126	500	10000	dimethyl trisulfide, $C_2H_6S_3^+$
30	NO^+	136	500	10000	alpha-pinene, $C_{10}H_{16}^+$
30	NO^+	146	500	10000	hexanoic acid, $C_6H_{12}O_2.NO^+$
30	NO^+	156	500	10000	dimethyl sulfate, $C_2H_6O_4S.NO^+$
30	NO^+	158	500	10000	dimethyl tetrasulfide, $C_2H_6S_4^+$
32	O_2^+	17	500	10000	ammonia, NH_3^+
32	O_2^+	18	500	10000	ammonia, NH_4^+
32	O_2^+	32	500	10000	$O_2^+(0)$
32	O_2^+	34	500	10000	hydrogen sulfide, H_2S+
32	O_2^+	35	500	10000	ammonia, $NH_3^+.H_2O$
32	O_2^+	36	500	10000	ammonia, $NH_4^+.H_2O$
32	O_2^+	43	500	10000	acetone, $C_2H_3O^+$
32	O_2^+	45	500	10000	formic acid, $HCOO^+$
32	O_2^+	48	500	10000	methyl mercaptan, CH_4S^+
32	O_2^+	57	500	10000	propanal, $C_3H_5O^+$
32	O_2^+	58	500	10000	acetone, $C_3H_6O^+$
32	O_2^+	58	500	10000	propanal, $C_3H_6O^+$
32	O_2^+	60	500	10000	carbonyl sulfide, COS^+
32	O_2^+	60	500	10000	butanoic acid, CH_3COOH^+
32	O_2^+	62	500	10000	dimethyl sulfide, $(CH_3)_2S^+$
32	O_2^+	74	500	10000	propanoic acid, $C_2H_5COOH^+$
32	O_2^+	88	500	10000	butanoic acid, $C_3H_7COOH^+$
32	O_2^+	93	500	10000	alpha-pinene, $C_7H_9^+$
32	O_2^+	94	500	10000	dimethyl disulfide,

Reagent m/z	Reagent	Product	Time limit in ms	Count limit	Comment
					$(CH_3)_2S_2^+$
32	O_2^+	94	500	10000	dimethylsulfone, $C_2H_6O_2S^+$
32	O_2^+	95	500	10000	dimethylsulfone, $C_2H_7O_2S^+$
32	O_2^+	96	500	10000	dimethyl sulfate, $CH_4O_3S^+$
32	O_2^+	122	500	10000	benzoic acid, $C_7H_6O_2^+$
32	O_2^+	126	500	10000	dimethyl trisulfide, $C_2H_6S_3^+$

Table 7: Details of the SIFT-MS settings of the method RedoxScreening S2-S11.sme with 4 measurement repetitions each.

reagent m/z	reagent	from m/z	to m/z	Step m/z	Time limit in ms	Count limit
19	H_3O^+	15	150	1	1000	10000
19	H_3O^+	35	35	1	5000	10000
19	H_3O^+	49	49	1	5000	10000
19	H_3O^+	63	63	1	5000	10000
30	NO^+	15	150	1	1000	10000
32	O_2^+	15	150	1	1000	10000
32	O_2^+	34	34	1	5000	10000
32	O_2^+	48	48	1	5000	10000
32	O_2^+	60	60	1	5000	10000
32	O_2^+	62	62	1	5000	10000

A2 Soil screening

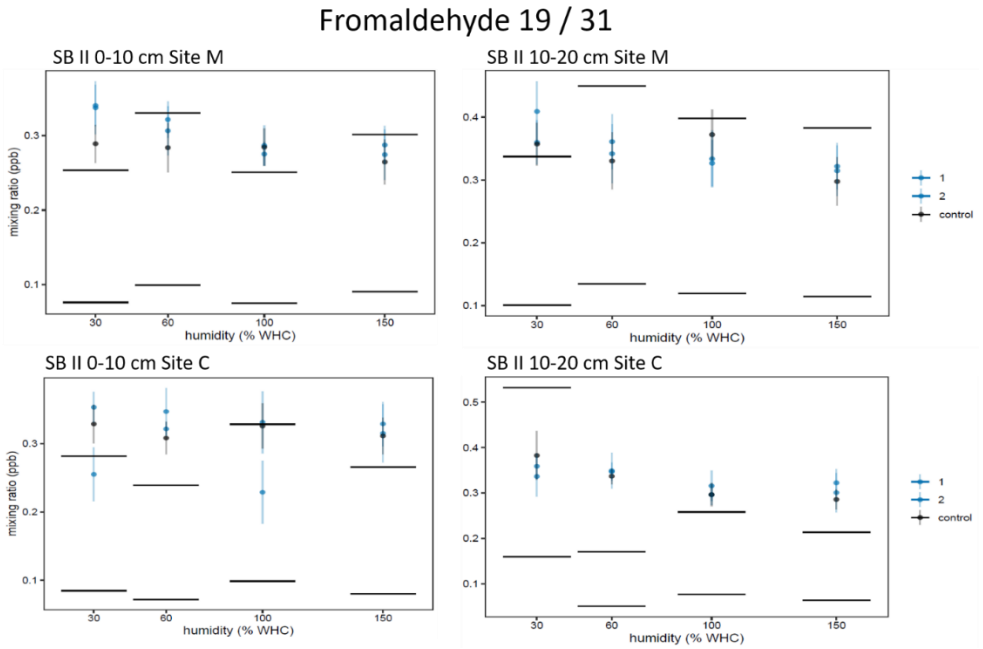

Figure 40: Comparison of formaldehyde emissions from different soils with different iron and water contents.

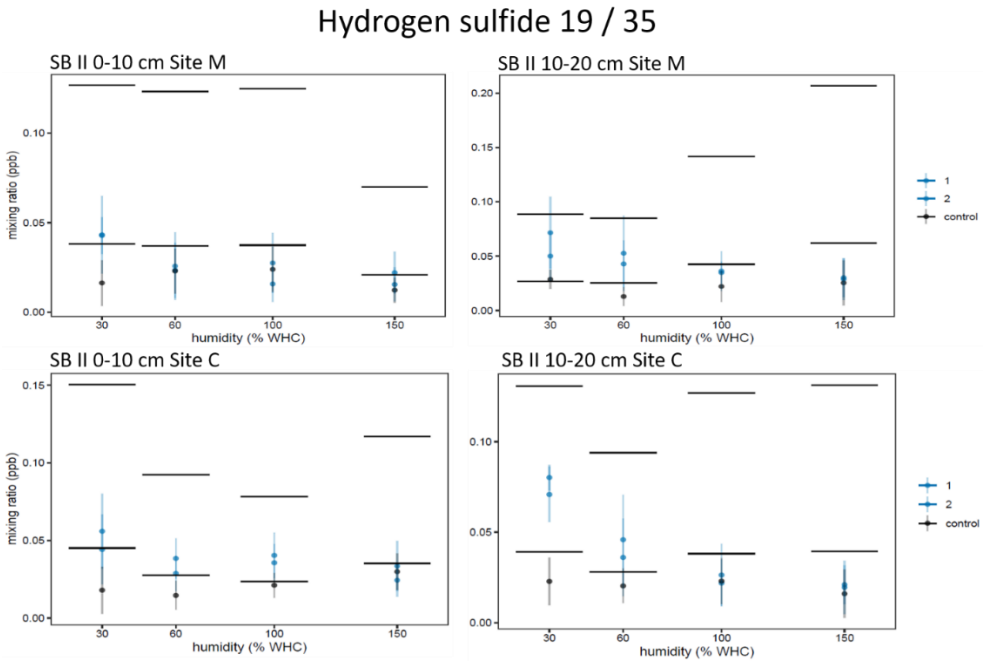

Figure 41: Comparison of hydrogen sulfide emissions from different soils with different iron and water contents.

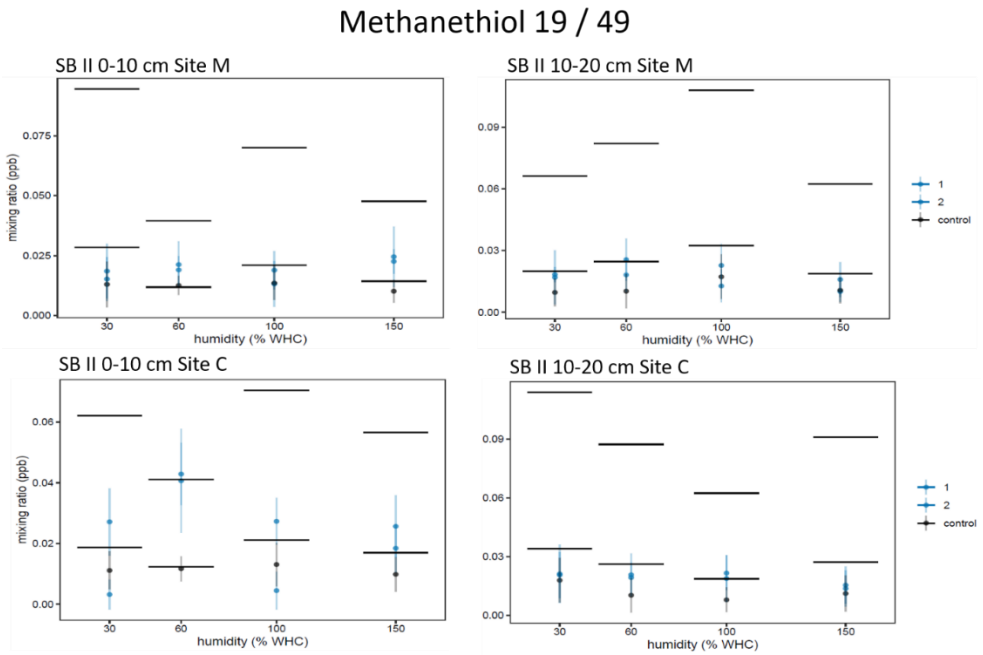

Figure 42: Comparison of methanethiol emissions from different soils with different iron and water contents.

A3 Comparison of oxic and anoxic incubation

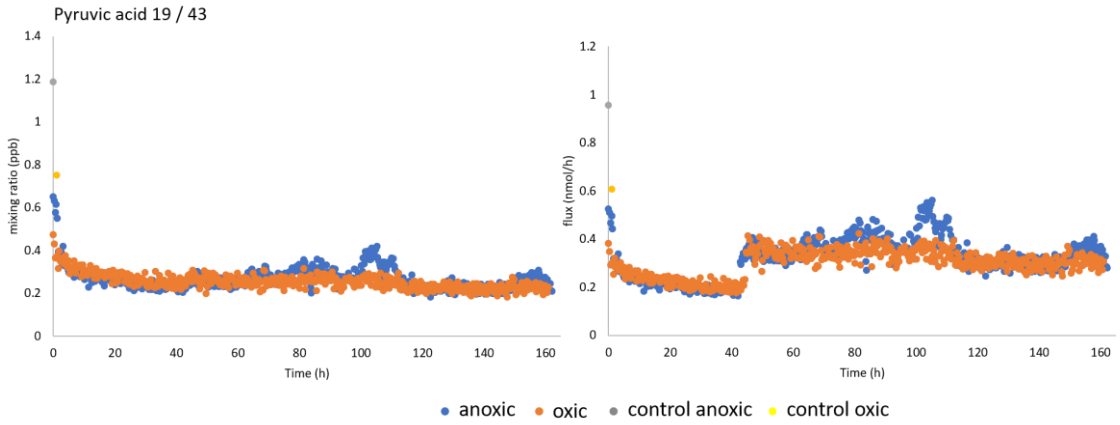

Figure 43: Course of pyruvic acid emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

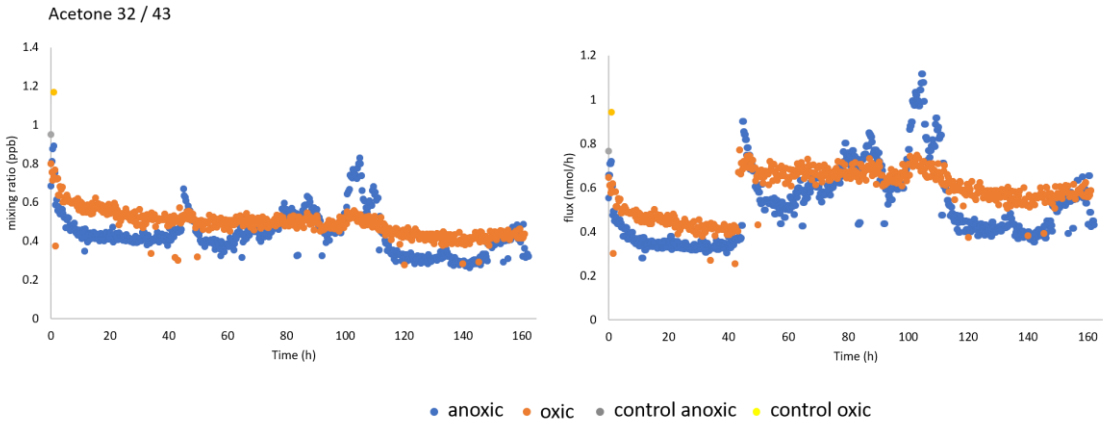

Figure 44: Course of acetone emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

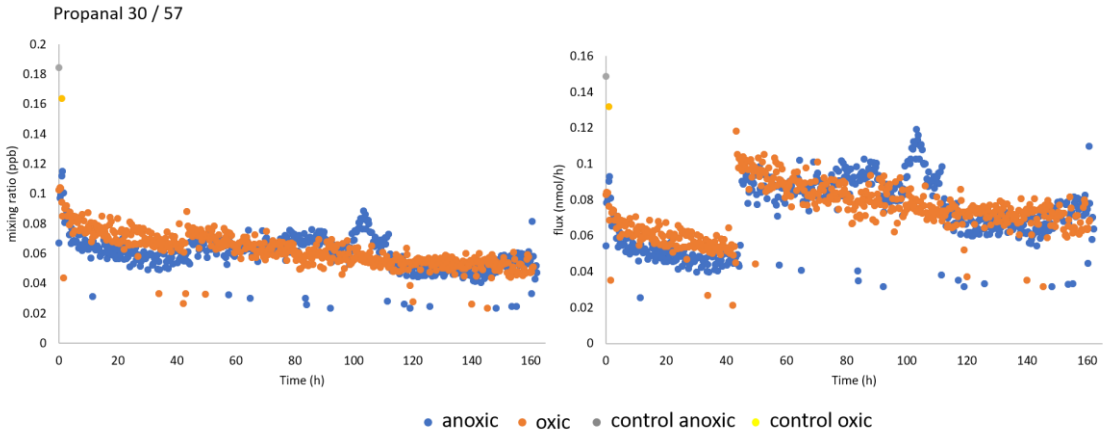

Figure 45: Course of propanal emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

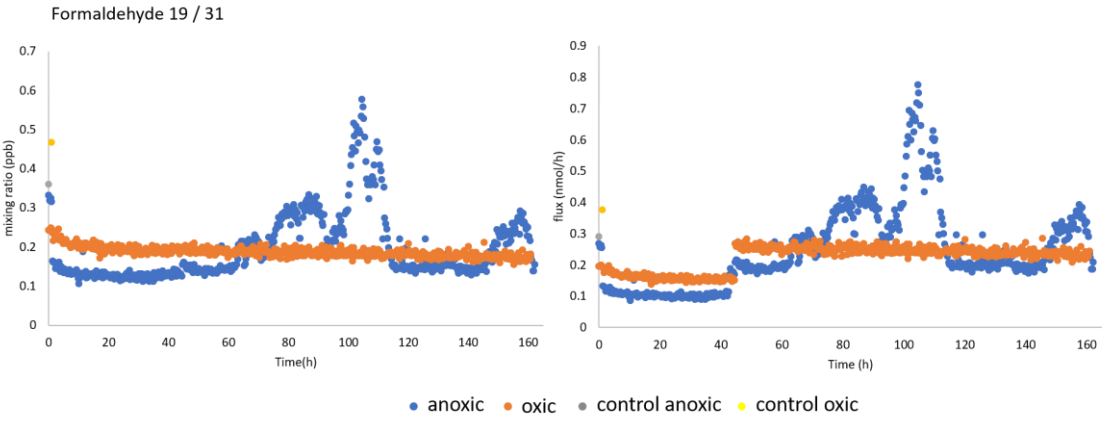

Figure 46: Course of formaldehyde emissions (mixing ratio and flux) over time during anoxic (N_2) and oxic (VOC free air) incubation. Soil: SB II 10-20 cm site "M", gas flow: 500 ml/min, 300 ml/min (after ca. 48 h).

A4 Drying experiments

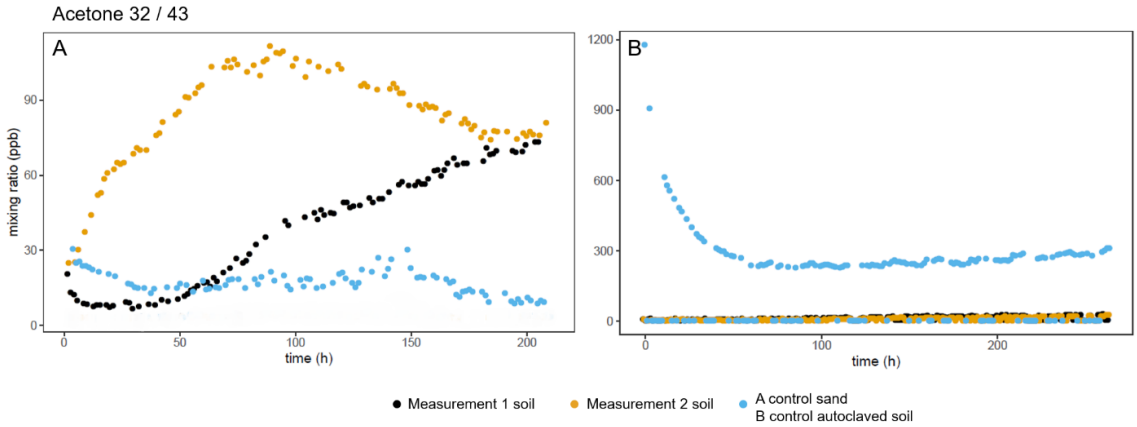

Figure 47: Time course of the acetone emissions of the two drying experiments (A and B) over the drying period. Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

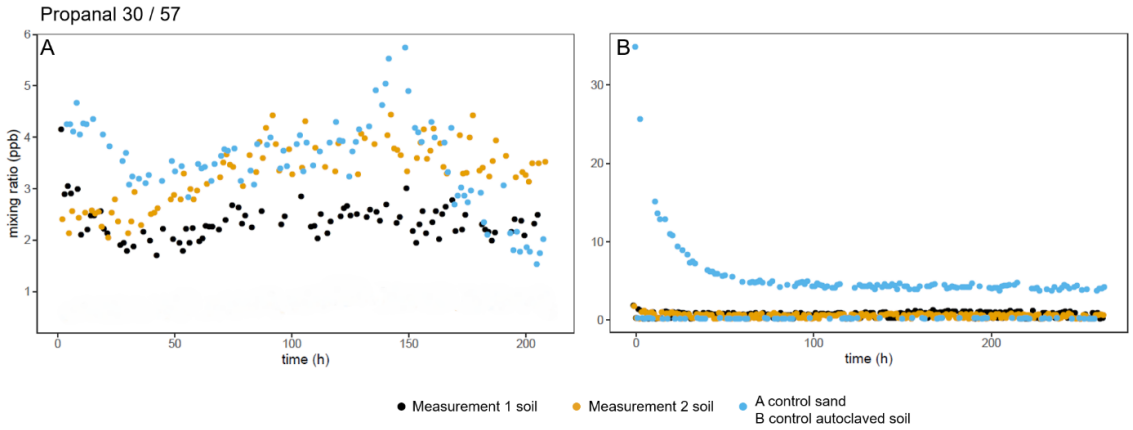

Figure 48: Time course of the propanal emissions of the two drying experiments (A and B) over the drying period. Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

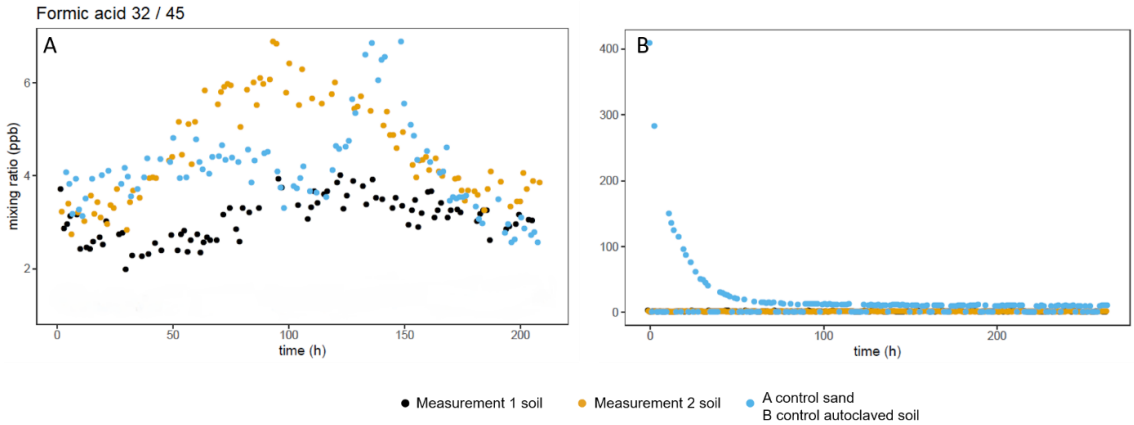

Figure 49: Time course of the formic acid emissions of the two drying experiments (A and B) over the drying period. Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

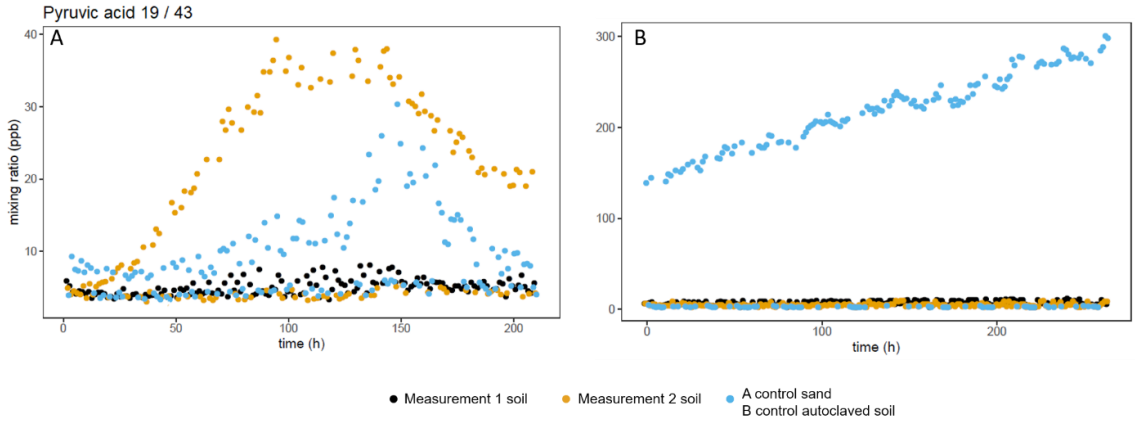

Figure 50: Time course of the pyruvic acid emissions of the two drying experiments (A and B) over the drying period. Gas flow: 300 ml/min (A) 200 ml/min (B), water added: 15 ml (A) 50 ml (B). The erroneous values which were caused by a malfunction of the SIFT-MS inlet have been removed from the graphic.

A5 Oxygen free incubation experiment

Table 8: Data of the gaschomatographic analysis of the headspace of every bottle for each time of the oxygen free incubation experiment.

Time in w	Sample	Compound	Peak area	Concentration in ppm	Concentration in ppb
	Ar background 1	CH_4			
		CO_2	1030229	275.94	
		N_2O	1285		217.19
	Ar background 1	CH_4			
		CO_2	1003204	268.25	
		N_2O	1268		213.86
	Ar background 1	CH_4	6365		
		CO_2	1276221	345.92	
		N_2O	1602		279.23
0	26	CH_4	44875	2.64	
		CO_2	6742487	1901.06	
		N_2O	1372		234.22
	7	CH_4	5295		
		CO_2	7929338	2238.72	
		N_2O	1255		211.32
	23	CH_4	5731		
		CO_2	6800124	1917.46	
		N_2O	1410		241.65

Time in w	Sample	Compound	Peak area	Concentration in ppm	Concentration in ppb
	25	CH_4	216976	13.59	
		CO_2	15789704	4474.97	
		N_2O	4898		924.24
	10	CH_4	5897		
		CO_2	7872662	2222.59	
		N_2O	1331		
	27	CH_4	84657	5.17	
	autoclaved	CO_2	40207641	11421.81	
		N_2O	5926		1125.41
1	2	CH_4	384097	21.43	
		CO_2	22346057	6314.81	
		N_2O	1127		136.34
	24	CH_4	433395	24.20	
		CO_2	17432343	4910.38	
		N_2O	1283		166.65
	5	CH_4	350580	19.54	
		CO_2	18231212	5138.71	
		N_2O	1248		159.85
	3	CH_4	215418	11.92	
		CO_2	15302127	4301.53	
		N_2O	1316		173.07
	13	CH_4	177917	9.81	
		CO_2	11323141	3164.26	
		N_2O	1371		183.75
	19	CH_4	95290	5.16	
	autoclaved	CO_2	30993052	8786.27	
		N_2O	5455		977.36
2	14	CH_4	1119890	87.40	
		CO_2	15616458	5942.08	
		N_2O	1332		219.26
	1	CH_4	1807319	141.19	

		CO_2	21502955	8217.90	
		N_2O	1197		182.07
	6	CH_4	220540	17.03	
		CO_2	7214257	2693.65	
		N_2O	1437		248.18
	28	CH_4	677901	52.82	
		CO_2	14782574	5619.69	
		N_2O	1330		218.71
	22	CH_4	682729	53.20	
		CO_2	11307502	4276.17	
		N_2O	1378		231.93
	21	CH_4	29028	2.05	
	autoclaved	CO_2	8878813	3337.20	
		N_2O	1521		271.33
3	30	CH_4	1328320	103.71	
		CO_2	21078344	8055.67	
		N_2O	1140		166.37
	8	CH_4	1874543	146.45	
		CO_2	20766484	7935.10	
		N_2O	1136		165.26
	4	CH_4	35719	2.57	
		CO_2	1567924	512.62	
		N_2O	4980		1224.22
	9	CH_4	1748332	136.58	
		CO_2	24428897	9351.05	
		N_2O	1492		263.34
	16	CH_4	1516335	118.42	
		CO_2	18889906	7209.59	
		N_2O	1800		348.18
	18	CH_4	94752	7.19	
	autoclaved	CO_2	23719261	9076.70	
		N_2O	3377		782.62
4	12	CH_4	153944	11.82	

	CO_2	59940846	23080.57	
	N_2O	39617		10766.09
15	CH_4	8903434	696.45	
	CO_2	59547014	22928.31	
	N_2O			
29	CH_4	4710835	368.39	
	CO_2	49513326	19049.12	
	N_2O			
17	CH_4	8532691	667.44	
	CO_2	52186173	20082.49	
	N_2O			
11	CH_4	9503157	743.37	
	CO_2	51552954	19837.67	
	N_2O			
20	CH_4	6423087	502.36	
autoclaved	CO_2	49301776	18967.33	
	N_2O			
Ar	CH_4			
background	CO_2	1030229	275.94	
1	N_2O	1285		217.19
Ar	CH_4			
background	CO_2	1003204	268.25	
2	N_2O	1268		213.86
Ar	CH_4	6365		
background	CO_2	1276221	345.92	
3	N_2O	1602		279.23
Room air 1	CH_4	45385	2.67	
	CO_2	1599582	437.92	
	N_2O	1503		259.85
Room air 2	CH_4	45339	2.67	
	CO_2	1611171	441.22	
	N_2O	1470		253.40
Room air 3	CH_4	45182	2.66	

	CO_2	1555748	425.45	
	N_2O	1488		256.92

Table 9: Data of the pH extraction of the soil samples from the different bottles at the various time points.

Time in w	Sample	Weight in g	pH (H_2O)
1	25	9.77	4.46
	26	10.31	4.62
	7	9.99	4.58
	23	10.30	4.38
	10	10.31	4.53
	27 autoclaved	9.95	4.05
	Control water		4.49
2	2	10.13	4.71
	24	10.07	4.67
	13	10.21	4.68
	5	10.13	4.66
	3	10.36	4.65
	19 autoclaved	10.29	4.11
	Control water		5.71
3	14	10.23	4.96
	1	10.16	4.61
	6	10.26	4.74
	28	10.28	4.72
	22	10.12	4.65
	21 atoclaved	10.35	4.12
	Control water		6.01
4	30	10.20	4.60
	8	10.60	4.85
	4	10.41	4.92
	9	10.70	4.73
	16	10.69	4.72
	18 autoclaved	10.32	4.05
	Control water		5.57

Time in w	Sample	Weight in g	pH (H_2O)
5	15	10.17	4.53
	29	10.25	4.65
	17	10.25	4.51
	11	10.09	4.52
	20	10.29	4.47
	12 autoclaved	10.10	3.98
	Control water		5.60

Table 10: Water content, weight, redox potential and nitrite content of the different soil samples in each of the bottles.

Time in w	Sample	Weight in g	Gas flow in ml/min	Water content in %	Redox potential in mV	Nitrite content in µg/l
0	26	119.62	102.1	5.88		too low
	7	119.69	100.7	4.87		too low
	23	116.48	99.3	5.47		too low
	25	119.79	102.1	5.72		too low
	10	118.10	100.7	4.16		too low
	27 autoclaved	120.0	99.3	3.11		too low
	Sand	120.0	100.7			
1	2	126.72	120.0	4.62		too low
	24	122.01	110.0	4.94		too low
	5	122.60	106.0	5.85		too low
	3	117.92	120.0	5.07		too low
	13	120.92	110.0	6.17		too low
	19 autoclaved	120.55	106.0	4.00		too low
	Sand	120.0	120.0			
2	14	125.54	120.0	6.17		8
	1	120.81	105.0	4.52		5
	6	123.24	112.0	5.52		4
	28	123.53	120.0	5.09		5
	22	123.07	105.0	4.60		5
	21 autoclaved	118.70	112.0	4.30		12

Time in w	Sample	Weight in g	Gas flow in ml/min	Water content in %	Redox potential in mV	Nitrite content in µg/l
	Sand	120.0	120.0			
3	30	121.84	108.5	5.66	368	5
	8	120.61	110.8	12.52	341	6
	4	125.96	100.0	7.04	329	5
	9	121.55	108.5	5.90	337	4
	16	121.03	110.8	6.69	333	5
	18 autoclaved	124.61	100.0	5.27	375	9
	Sand	120.0	108.5			
4	15	124.13	110.0	5.44	345	8
	29	94.57	104.0	5.93	338	5
	17	123.33	110.0	6.81	331	6
	11	119.46	110.0	6.46	331	5
	20	120.11	104.0	6.18	340	8
	12 autoclaved	120.83	110.0	5.84	346	5
	Sand	120.0	110.0			

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Declaration of authorship

I, hereby certify that I have researched and written this Master thesis myself, no passages of text have been taken from third parties or my own examination papers without having been identified as such and that all tools, personal notification and sources used have been indicated. The assistant and professional consultant was not utilized and third parties have neither directly or indirectly received monetary benefits from the candidate for work related to the contents of the submitted Master thesis.

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