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Key Points:
- Elevated CO_2 at potentially ambient soil pore levels leads to a decrease of carbonyl sulfide uptake
- CO_2 concentrations in soil pores up to 7600 ppm might cause competitive inhibition of RubisCO but not CA or PEPCO
- Antimicrobial treatment changes soil atmosphere OCS exchange and suggests that fungi play a dominant role

Supporting Information:
- Supporting Information S1
- Data S1

Correspondence to:
R. Bunk and J. Kesselmeier,
r.bunk@mpic.de;
j.kesselmeier@mpic.de

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Exchange of carbonyl sulfide (OCS) between soils and atmosphere under various CO_2 concentrations

Rüdiger Bunk[1], Thomas Behrendt[2], Zhigang Yi[3], Meinrat O. Andreae[1], and Jürgen Kesselmeier[1]

[1]Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany, [2]Biogeochemical Processes Department, Max Planck Institute for Biogeochemistry, Jena, Germany, [3]College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou, China

Abstract A new continuous integrated cavity output spectroscopy analyzer and an automated soil chamber system were used to investigate the exchange processes of carbonyl sulfide (OCS) between soils and the atmosphere under laboratory conditions. The exchange patterns of OCS between soils and the atmosphere were found to be highly dependent on soil moisture and ambient CO_2 concentration. With increasing soil moisture, OCS exchange ranged from emission under dry conditions to an uptake within an optimum moisture range, followed again by emission at high soil moisture. Elevated CO_2 was found to have a significant impact on the exchange rate and direction as tested with several soils. There is a clear tendency toward a release of OCS at higher CO_2 levels (up to 7600 ppm), which are typical for the upper few centimeters within soils. At high soil moisture, the release of OCS increased sharply. Measurements after chloroform vapor application show that there is a biotic component to the observed OCS exchange. Furthermore, soil treatment with the fungi inhibitor nystatin showed that fungi might be the dominant OCS consumers in the soils we examined. We discuss the influence of soil moisture and elevated CO_2 on the OCS exchange as a change in the activity of microbial communities. Physical factors such as diffusivity that are governed by soil moisture also play a role. Comparing K_M values of the enzymes to projected soil water CO_2 concentrations showed that competitive inhibition is unlikely for carbonic anhydrase and PEPCO but might occur for RubisCO at higher CO_2 concentrations.

1. Introduction

Carbonyl sulfide (OCS) is a sulfur-containing trace gas with an atmospheric concentration of about 500 ppt [Carroll, 1985]. More recently, *Montzka et al.* [2007] reported an atmospheric concentration of 476 ± 4 ppt for the Northern Hemisphere. Terrestrial vegetation is regarded as the main global sink for OCS. Within this context, there is an increasing interest to use OCS as a proxy for CO_2 to study ecosystem or global CO_2 fluxes, exploiting the parallels between CO_2 and OCS uptake by plants. As reported earlier, the same enzymes that are responsible for the uptake of CO_2 in plants, i.e., phosphoenolpyruvate carboxylase (PEPCO), ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCO), and carbonic anhydrase (CA), are also the key players for the uptake of OCS [*Protoschill-Krebs and Kesselmeier*, 1992; *Protoschill-Krebs et al*., 1996; *Blezinger et al*., 2000; *Sandoval-Soto et al*., 2005]. This enzymatic model, consisting of three enzymes, assigns a key role to CA and has been confirmed recently by *Stimler et al.* [2011]. Because CA is involved in the exchange of CO_2 in plants, animals, fungi, and microorganisms alike, OCS should be decomposed in almost all living cells. Furthermore, *Ogawa et al.* [2013] identified an enzyme with high similarities to CA in *Thiobacillus thioparus* strain THI 115, which has similar OCS degrading abilities as CA but much lower reactivity with CO_2. In addition to PEPCO, RuBisCO, COSase, and CA, another enzyme using OCS as substrate is nitrogenase [*Seefeldt et al*., 1995].

Given the high similarity in the uptake resistance for CO_2 and OCS, *Goldan et al.* [1988] suggested that the uptake ratio of these two gases should be equal to the ratio of their respective atmospheric mixing ratios of about 1.3×10^{-6}. This quantitative link between OCS uptake and terrestrial primary productivity was further developed by *Chin and Davis* [1993]. Based on the aforementioned discoveries regarding OCS uptake via the key enzymes of assimilation by *Protoschill-Krebs and Kesselmeier* [1992], *Chin and Davis* [1993] used a ratio of deposition velocities for CO_2 and OCS of 1 to quantify the uptake of OCS by terrestrial vegetation from the atmospheric ratios of these two atmospheric gases, effectively linking the terrestrial uptake of OCS to the

net photosynthetic production (NPP) of an ecosystem. To include the preferred uptake of OCS over CO_2 at leaf and enzyme level [*Kesselmeier and Merk*, 1993; *Protoschill-Krebs et al*., 1996], *Sandoval-Soto et al.* [2005] recalculated the ratios for most major ecotypes, taking into account the deposition velocities of OCS and CO_2, and found them almost exclusively to be greater than 1. Furthermore, they concluded that calculations of OCS uptake should not be based on NPP but on gross primary production (GPP) instead, as the uptake of OCS into vegetation is unidirectional and OCS is irreversibly split into H_2S and CO_2 within plants. This model was confirmed by *Campbell et al.* [2008], who demonstrated that such a GPP-driven model fits the OCS modeled data much better to the measured values.

There is an increasing interest now in exploiting the close relationship between OCS and CO_2 uptake to use OCS as a proxy for the estimation of ecosystem GPP [*Asaf et al*., 2013; *Berry et al*., 2013; *Berkelhammer et al*., 2014]. The potential, limitations, and requirements of this prospect are discussed in detail in a review by *Wohlfahrt et al.* [2012]. However, unidirectional uptake of OCS by plants may be questioned, as *Bloem et al.* [2012] observed OCS emission from oilseed rape plants infected with a pathogenic fungus. As such infections are widespread, such behavior might be an additional complication for the OCS/CO_2 approach. Additionally, the role of other flux contributors (such as soils) is one of the largest question marks regarding the use for OCS as a CO_2 proxy, which might result in a complex mixture of exchange processes and limit its usefulness.

Soils are known to have the potential to be either sources or sinks of OCS, depending on the soil quality and source, and on various factors such as atmospheric OCS concentration, temperature, or soil water content [*Kesselmeier et al*., 1999; *Van Diest and Kesselmeier*, 2008; *Maseyk et al*., 2014; *Whelan and Rhew*, 2015]. Of special interest is the light-dependent and obviously abiotic OCS production reported by *Whelan and Rhew* [2015]. Two biotic sources have been reported, production from thiocyanate by thiocyanate hydrolase [*Katayama et al*., 1992; *Katayama et al*., 1998] and production from carbon disulfide by carbon disulfide hydrolase [*Smith and Kelly*, 1988; *Smeulders et al*., 2011]. *Lehmann and Conrad* [1996] also observed an increase of OCS emission from soils after the addition of thiocyanate. As the bacteria used by the above-mentioned authors can be found in soils, it is highly likely that these pathways are involved in OCS production by soils. Thiocyanate is expected to be found in soils because it is produced by glucosidase from mustard oil (glucosinolates) when plant cells become damaged [*Wood*, 1975, *Bones and Rossiter*, 2006, *Halkier and Gershenzon*, 2006, *Morant et al*., 2008].

Atmospheric CO_2 concentrations have been rising ever since the industrial revolution and are expected to keep going up in the future. This will not only affect the CO_2 uptake by vegetation but also the exchange of OCS. As OCS and CO_2 are binding to the same active center of CA [*Notni et al*., 2007], RuBisCO [*Lorimer and Pierce*, 1989], and possibly also PEPCO, it can be assumed that these substrates are in competition with each other. Little is known about the development of the OCS sink under elevated CO_2. *Stimler et al.* [2010] saw no cross sensitivity between CO_2 and OCS during their measurements with various C3 plants, but there are a few reports about a decrease in the OCS uptake under elevated CO_2 [*White et al*., 2010; *Sandoval-Soto et al*., 2012]. As the typical CO_2 concentrations in soils are much higher than those tested in previous experiments with plants, the potential of competitive inhibition may be much stronger in soils. In this case, the capacity of soils to act as OCS sink would become difficult to predict. To examine the impact of CO_2 concentration on the OCS exchange, we measured exchange rates for five soils under five different CO_2 concentrations using an automated dynamic chamber system. According to the literature, soil CO_2 concentrations can easily reach thousands of parts per million even in the upper centimeters of soils, with CO_2 concentration usually increasing with depth [e.g., *Gerstenhauer*, 1972; *Kiefer and Amny*, 1992, and literature cited therein; *Hirano et al*., 2003; *Yonemura et al*., 2009; *Sakurai et al*., 2015]. In close accordance with these reports, we choose concentrations of up to 7600 ppm, the upper limit for the OCS instrument used for our measurements. Our experiments aimed to improve our understanding on how soil moisture and atmospheric CO_2 concentration influence the OCS exchange of soils and whether biotic processes are involved in this exchange.

2. Materials and Methods

2.1. Soil Origin, Handling, Storage, and Experimental Practice

Five different soils were used in our experiments: (1) "Mainz soil," an arable soil collected 2014 from a wheat field near Mainz-Finthen (49.95°N 8.25°E), Germany. Samples from this site have been collected and

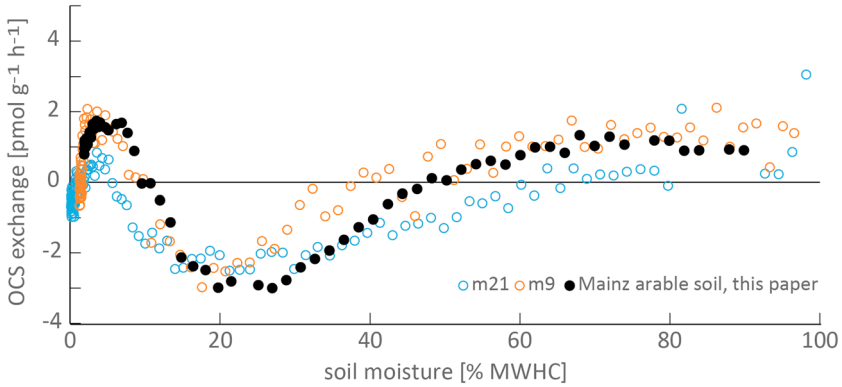

Figure 1. Carbonyl sulfide exchange for Mainz soil in two previous measurements (m21 and m9) and from this manuscript at similar conditions. Soil moisture is given as percent of the soil's maximum water holding capacity (MWHC, see section 2.5).

investigated already earlier [*Kesselmeier et al*., 1999; *Van Diest and Kesselmeier*, 2008]. (2) "Nördlingen sugar beet," an arable soil collected in April 2014 from an organically fertilized sugar beet field at the Nördlinger Ries, Germany, near Nördlingen (48.8883333°N 10.5358333°E). (3) "Nördlingen corn," an arable soil collected in April 2014 from a conventionally fertilized cornfield at the Nördlinger Ries (48.8883333°N 10.5358333°E). (4) "Suriname," a tropical rainforest soil collected (05.0763°N, −55.0029°E) in Suriname in 2012. (5) "Himalaya," an arable soil collected from a rice field (30.83480°N, 76.98631°E) in the Himalaya in 2014.

Soils can be very heterogeneous in structure, mineral composition, and microbial activities. Therefore, all soil samples investigated were thoroughly sieved and mixed in order to obtain a homogenous sample, which allowed a subsequent and highly reproducible sample withdrawal over time. To minimize microbial adaptations, the samples were stored in the refrigerator at 5°C to prevent (or slow down) any further development of microbial communities and nutrient content. This well-accepted approach allowed an incubation of soil samples starting at a comparable developmental stage at each step. No incubated soil sample was used twice. Experiments with an automated soil laboratory allowed us to measure four to five samples simultaneously against an empty chamber (see section 2.4.2). Hence, the different soil types were investigated simultaneously under identical conditions, delivering consistent data sets covering the conditions from 100% water holding capacity (WHC) to dryness. When measurements came to an end and soil samples reached a dry condition, samples were exchanged against new ones for the stepwise incubation under different CO_2 regimes.

We found a very close agreement when measuring a few samples from the sample soil pool again under identical conditions. Figure 1 shows the replicated OCS exchange as observed under 440 ppm CO_2. This performance of the Mainz arable soil compares well with that from a few months earlier (unpublished data). Conditions (cycle time, flushing rate, temperature) for m9 and m21 differed slightly from the measurements presented in this study.

Table 1 summarizes soil properties such as content of NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, total carbon, total nitrogen, total sulfur, pH, loss on ignition, and particle density, as determined by Envilytix (Wiesbaden, Germany).

2.2. Dynamic Chamber System

The automated dynamic chamber system has been described in detail in *Behrendt et al.* [2014]. In short, it consists of four main units developed by our institute: (1) the gas dilution unit, which generates the air with

Table 1. Properties of the Investigated Soil Samples (PD is Particle Density, LOI is Loss on Ignition)

Sample	NH_4^+ [mg kg^{-1}]	NO_2^- [mg kg^{-1}]	NO_3^- [mg kg^{-1}]	SO_4^{2-} [mg kg^{-1}]	PO_4^{3-} [mg kg^{-1}]	C [%]	N [%]	S [%]	pH —	LOI [%]	PD [g cm^{-3}]
Mainz	<0.05	0.07	3.78	65.0	0.05	2.5	0.17	0.03	7.6	3.7	2.6
Nördlingen corn	<0.1	0.01	86.0	2.58	5.94	1.6	0.21	0.03	7.1	5.1	2.6
Nördlingen sugar beet	1.6	0.17	75.6	17.56	10.72	1.6	0.20	0.04	7.2	4.9	2.6
Himalaya	1.9	0.03	402.8	22.26	112.76	3.0	0.33	0.06	7.4	8.7	2.5
Suriname	68.9	<0.01	360.6	47.18	0.42	8.7	0.56	0.07	3.9	18.3	2.3

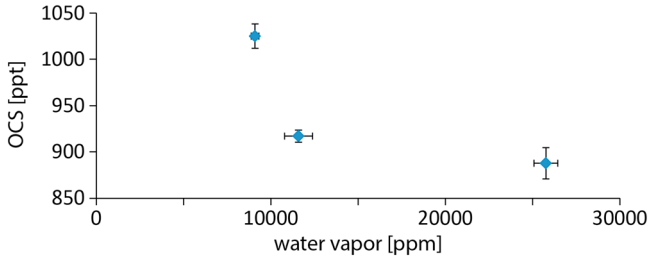

Figure 2. Apparent OCS mixing ratio measured at three different water vapor concentrations. The same sample gas was humidified using a Nafion dryer in reverse mode (transferring water vapor through the Nafion mesh from the flushing air which had a higher water vapor concentration than the gas sample in the inner tube).

desired qualities (relative humidity, trace gas concentrations) for flushing the soil chambers; (2) the thermostat valve unit, regulating the flow of flushing air through the soil chambers and selecting from which chamber the air is fed to the analyzer unit by computer-controlled Galtec valves (Entegris, Billercia, model Nr. 203-3414-215); (3) the thermostat cabinet unit, housing up to seven Plexiglas chambers and regulating their temperature; and (4) the analyzer unit, consisting of the chosen set of analyzers. The setup allows connecting various analyzers, tailored to the needs of the individual experiment. In this case an nondispersive infrared CO_2/H_2O analyzer (LiCOR 840A, LiCOR Inc., USA) and an OCS/CO_2 analyzer (described below) were used. A flushing air stream with the desired concentration of water vapor, OCS, and CO_2 was generated in the gas dilution unit, then directed by the thermostat valve unit into the thermostat cabinet unit. There, the cuvettes (five samples and one empty reference) were flushed with this air stream at set rates. Samples were drawn by the analyzer units to determine the trace gas concentrations. Only the dynamic mode described in *Behrendt et al.* [2014] was used. A cylinder of compressed gas (500 ppb OCS in nitrogen, Air Liquide, Germany) and a cylinder of pure CO_2 (4.5, Air Liquide, Germany) were connected via two Mass Flow Controllers (MKS Instruments, Germany) to the system, allowing the addition of controlled amounts of OCS and CO_2 to the flushing air stream.

2.3. OCS Analyzer and Cross Sensitivity to High CO_2 Concentration and to Water Vapor

Carbonyl sulfide concentrations were measured with a new laser-based instrument (LGR OCS/CO_2 analyzer model 907 0028, Los Gatos Research, USA). The LGR OCS analyzer uses cavity-enhanced absorption spectroscopy techniques (Off-Axis Integrated-Cavity Output Spectroscopy) where the laser wavelength is scanning selected absorption features of the target species. The measured absorption spectra recorded are corrected according to cell temperature and pressure and effective path length and are supposed to deliver a quantitative measurement of mixing ratios without external calibration. However, we checked the calibration and found that the OCS signal of the analyzer was strongly affected by the water vapor content of the measured air. This caused especially severe problems when the water content fluctuated because of evaporation or transpiration. A strong underestimation of OCS concentrations mimicked a spurious uptake. After initially noticing this effect in measurements and some simple tests, we confirmed it using a Nafion dryer (Model Perma Pure MD™-110, Perma Pure LLC, USA) in reverse mode (as suggested by LGR). A gas sample of known OCS concentration was humidified in steps by adding water vapor with a Dew Point generator to the flushing air in the outer tube of the Nafion dryer. Increasing water vapor caused a significant drop in the recorded OCS concentration, exceeding any possible dilution effect. The impact of the water vapor concentration on the apparent OCS concentration is shown in Figure 2. This bias is normally corrected by an algorithm, and other colleagues working with this model report no such problems [i.e., *Berkelhammer et al.*, 2014; *Belviso et al.*, 2016]. The problem may be individual to our instrument, which was one of the first ones built and was also adapted for measurements at high CO_2 concentrations. Therefore, all gas samples were dried by a Nafion dryer (Model Perma Pure MD™-110, Perma Pure LLC, USA) before entering the OCS analyzer. Dry compressed air was used for flushing of the outer tube. Under these conditions, the determination of OCS was sufficiently accurate and precise (see Table 2). Additionally, the analyzer was tested at the Forschungszentrum Jülich (FZJ, Germany) by measuring defined concentrations of OCS produced with a setup using permeation tubes. In addition, at low concentrations (ppt range), a NOAA Standard (449.8 ± 1.4 ppt, Essex stainless steel cylinder, cylinder number SX-3584, NOAA, USA) was measured. Measured and calculated OCS concentrations did fit very well for higher concentrations. Comparison to the NOAA standard showed an average

Table 2. Calculated and Measured Amount of CO_2 and OCS in Calibration Mixtures with Increasing CO_2

CO_2 Concentration (ppm)		CO_2 Recovery	OCS Concentration (ppt)		OCS Recovery
Calculated	Measured ± SD	%	Calculated	Measured ± SD	%
499	469 ± 1.01	94	533	539 ± 3.87	101
998	904 ± 2.58	91	533	534 ± 3.27	100
2988	2738 ± 10.1	92	532	544 ± 4.07	102
4970	4476 ± 4.97	90	531	531 ± 4.16	100
6945	6255 ± 6.55	90	530	526 ± 6.45	99
8911	7919 ± 4.88	89	528	515 ± 8.81	97

underestimation of 7%. Maximal underestimation was 10%. Consequently, measured fluxes might be underestimated by 7%.

To test for a possible interference of the Nafion dryer, OCS (500 ppb OCS in nitrogen, Air Liquide, Germany) was added to a dry air stream consisting of CO_2 in synthetic air (100 ppm, Air Liquide, Germany). One half was directly sent to the analyzer, the other half after passing a Nafion dryer. A three-way valve (stainless steel, SS-45XS12, Swagelok, USA) was used to switch between the sample streams. Measurements of OCS were not affected by the use of a Nafion dryer as shown in Figure 3.

The precision was found to be better than 5 ppt, and the detection limit defined as three times SD of the standard noise was around 35 ppt.

The influence (bias) of high CO_2 levels on the determination of OCS was tested by measurements with synthetic air, containing defined amounts of OCS and CO_2. A basic flow of 10 L min^{-1} of synthetic air was flushed through three glass bottles (5 L volume each, HWS Labortechnik, Germany) that were used as mixing devices and were equipped with a ring poppet valve (stainless steel, SS-4C-5, Swagelok, USA) opening at an overpressure of 35 kPa (5 psi) for safety reasons. Increasing amounts of pure CO_2 were added with flow rates between 5 and 90 mL min^{-1} via a mass flow controller (MKS). OCS was added from a cylinder with a compressed and certified gas mixture of OCS in nitrogen with a flow rate of 9.6 mL min^{-1}. An open junction just before the analyzer prevented overpressure within the instruments. The data from the first 5 min after the start of gas flow were discarded to account for an equilibration of the system, and the following 10 min average was used. The OCS and CO_2 concentrations are reported as calculated and measured values (Table 2). The recovery of OCS appears quantitative within experimental uncertainties under all conditions and matches the calculated values. There is a slight trend toward underestimation (3%) at higher CO_2, but the values remain within the error ranges of the mass flow controllers. The determination of CO_2 is accurate enough at normal concentrations, but we observed an underestimation with increasing CO_2, which however did not affect our measurements or interpretations.

2.4. Experimental Procedure

2.4.1. Mixing of Gases and Cuvette Flush

Cuvettes were flushed with a total flow of 2.4 L min^{-1} of compressed air purified by a pure-air generator (PAG 003, Ecophysics, Switzerland). To this flow, OCS and CO_2 were added via mass flow controllers to reach the

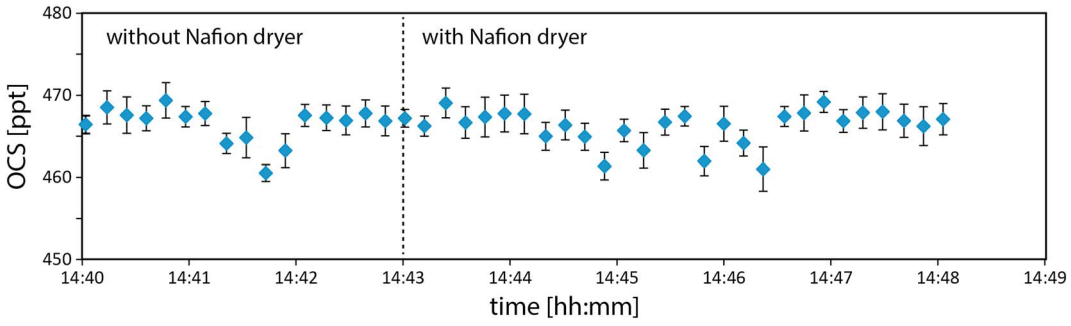

Figure 3. Measured OCS concentration (blue diamonds) in dry air with (right) and without (left) passing a Nafion dryer. Error bars denote the measurement uncertainty of the OCS/CO-Analyzer.

Table 3. Experiments Performed[a]

	Untreated Soils				
OCS [ppt]|| CO_2[ppm] Concentration	Mainz	Nördlingen Corn	Nördlingen Sugar Beet	Himalaya	Suriname
490 || 440(20)	x	x	x	x	x
490 || 990(20)	x	no sample	no sample	no sample	x
490 || 2000(20)	x	x	x	x	x
490 || 3850(20)	x	x	x	x	x
490 || 7600(70)	x	x	x	x	x
	Chloroform Sterilized Soils				
490 || 470(20)	x	x	x	x	x
490 || 1010(10)	x	x	no sample	no sample	x
490 || 2000(10)	x	x	x	no sample	x
490 || 4030(30)	x	x	x	no sample	x
490 || 7520(30)	x	x	x	x	x
	Antifungal or Antibiotic Mainz or Suriname				
OCS [ppt]|| CO_2[ppm] concentration	untreated	nystatin	streptomycin		
925 || 430(10)	x	x	x		

[a]The OCS||CO_2 column shows the average (whole experiment) OCS and CO_2 mixing ratios of OCS and CO_2. The SD of the average OCS mixing ratio was about 10 ppt (whole experiment), while the SD of the average CO_2 mixing ratio was more variable and is given in the bracket behind the mixing ratio.

desired mixing ratios. Source gases were compressed pure CO_2 (4.5, Air Liquide, Germany) and OCS, 500 ppb in nitrogen (Air Liquide, Germany).

2.4.2. Sample Treatment

There were three sets of experiments: "natural, nonsterilized," "$CHCl_3$ sterilized," and "antibacterial and antifungal inhibition." The procedures for each set are described below. To reach 100% WHC, the soils were wetted with milliQ-water (18 MΩ, ELGA-Purelab ultra ionic, Vivendi Water Systems Ltd, UK) to reach field capacity. The maximum water holding capacity was determined with the filter method described in *Behrendt et al.* [2014] using Whatman filter paper no. 42.

"Natural Nonsterilized Soils":

Samples of 60 g soil (except for the Suriname soil with 20 g) were put into the chamber and wetted to the maximum water holding capacity. Chambers were flushed with dry air, containing 490 ppt OCS and either 440(±20), 990(±20), 2010(±20), 3850(±30), or 7600(±70) ppm CO_2. The basis for the flushing air was compressed, dry ambient air. The pure air generator did not fully remove background CO_2, resulting in small fluctuations in the CO_2 mixing ratio. These changes happened gradually over time, usually not more than 5 ppm h^{-1}. Above, and in Table 3, the average for the whole experiment is given, with its standard deviation (±SD) in brackets. To better reflect these gradual changes, reference concentrations between sets of measurements were interpolated as described in section 2.5. Trace gas concentrations in five sample chambers and one empty reference chamber were measured in a repeating sequence, while the samples were gradually dried out by the dry flushing air. When water evaporation ceased, the air-dried samples were weighed and fully dried at 105°C for 24 h, then weighed again to determine the dry weight.

"$CHCl_3$ Fumigated":

Chloroform fumigation affects fungi, bacteria, and protozoans in soil samples. While protozoans are killed completely, usually a small portion of fungal and bacterial populations remains active. Furthermore, fungi are less sensitive than bacteria. [*Ingham and Horton*, 1987]. Of the sample, 60 g (20 g in case of the Suriname soil) was exposed to the vapor of 300 μL chloroform for 48 h in a desiccator. For the 470 ppm experiment, the exposure time was 24 h, and 200 μL chloroform was used. After fumigation with $CHCl_3$, the samples were wetted and incubated as described for "natural" measurements. As described under "natural nonsterilized soils" above, CO_2 mixing ratios varied slightly resulting in 470(±20), 1010(±10), 2000(±10), 4030(±30), and 7520(±30) ppm. Due to the lack of sufficient soil, no $CHCl_3$-fumigated experiments could be performed for the "Himalaya" soil at 1010, 2000, and 4030 ppm CO_2, as well as for "Nördlingen sugar beet" soil at 1010 ppm CO_2.

"Treatment With Antifungal and Antibiotic Compounds":

Streptomycin is an antibiotic that acts against Gram-negative and Gram-positive bacteria by binding to the 30S ribosomal subunit. At the concentration used (200 μg L^{-1}), streptomycin is usually not a potent agent against fungi, requiring roughly a thousand-fold concentration of streptomycin (3.5–8 mg mL^{-1}) to be effective [*Robinson et al*., 1944, *Robinson*, 1946]. Nystatin is mainly active against most fungi, while bacteria are not affected [*Lampen et al*., 1957]. It acts by binding to the membranes of sensitive organisms making them permeable for cations [*Kinsky*, 1962]. Five samples each of Mainz soil and Suriname soil were treated with nystatin or streptomycin, or left untreated. Measurements were performed at 925 ppt OCS and 430 (±15) ppm CO_2 in the flushing air. Nystatin and streptomycin inhibition was performed in the course of the wetting procedure by adding 100 μg L^{-1} nystatin solution or 200 μg L^{-1} streptomycin solution instead of pure water. Table 3 shows an overview of all performed experiments.

2.5. Calculations

Continuous changes of the gravimetric soil moisture were calculated according to *Behrendt et al.* [2014], based on the calculation of the mass balance for evaporated water, which was monitored by a LiCOR 840A, thus getting a continuous track of soil water content. Soil moisture, given in percent of maximum water holding capacity (MWHC), was derived from the gravimetric soil moisture according to equation (1).

$$\mathrm{SM} = \frac{\theta_{t_i}{}^{*}}{\theta_{\max}} 100 \tag{1}$$

where θ_{ti} is the gravimetric soil moisture at any given time, $\theta_{\max}$ is the gravimetric soil moisture directly after wetting, and SM is the soil water content in percent of the respective soil's maximum water holding capacity.

Emission rates, J [pmol g^{-1} h^{-1}], were calculated based on the chamber flushing rates, Q [mol h^{-1}], the dry weight of the soil sample (m_{soil} [g]), and the difference of OCS concentration between sample and reference chamber ($\mathrm{OCS_s}$ [pmol mol^{-1}] − $\mathrm{OCS_r}$ [pmol mol^{-1}]) following equation (2).

$$J = \frac{(\mathrm{OCS_s} - \mathrm{OCS_r}) \times Q}{m_{\mathrm{soil}}} \tag{2}$$

Our OCS/CO_2 analyzer, like most instruments of its kind, has only one measurement channel. Therefore, the trace gas concentrations in the air from the dynamic chambers were measured in sequential cycles. Each cycle started with the reference chamber, followed by the sample chambers. Each chamber was measured for 10 min. Thus, one measurement cycle lasted 50 to 60 min, depending on how many sample chambers were used. The reference data for a given time, t_i, was calculated from the measured reference data by linear interpolation according to equation (3).

$$f(t_i) = f_0 \times \frac{t_1 - t}{t_1 - t_0} + f_1 \times \frac{t - t_0}{t_1 - t_0} \tag{3}$$

Here $f(t_i)$ is the trace gas concentration at time t_i, and f_0 is the trace gas concentration at the last reference measurement before t_i, while f_1 is the trace gas concentration at the reference measurement following t_i and t_0 is the time at which f_0 was measured. Finally, t_1 is the time at which f_1 was measured.

To account for disturbances when switching from one chamber to the next, only those 150 s (of the 600 s) of a measurement period per chamber was used when the fluxes through the chamber had stabilized. The first 390 s after switching to another chamber and the last 60 s before switching were ignored. With this procedure, the fluctuations of the OCS concentration in the reference chambers' flushing air were less than 1%.

High, optimal, and low moisture ranges were defined qualitatively based on the correlation of OCS exchange rates and soil moisture, placing the border between the three ranges at the intersection of OCS exchange with the x axis (compromising between all CO_2 concentration sets) as illustrated in Figure 4. These exchange rates were fitted with the multipeak curve-fitting tool of Origin Pro 9 and each moisture range integrated by the trapezoid integration approach according to equation (4):

$$A = (\mathrm{MWHC_d} - \mathrm{MWHC_w}) \times \frac{J_{\mathrm{MWHC_w}} + J_{\mathrm{MWHC_d}}}{2} \tag{4}$$

where A is the area of a given trapezoid, $\mathrm{MWHC_d}$ is the soil water content at the drier point, $\mathrm{MWHC_w}$ is the soil

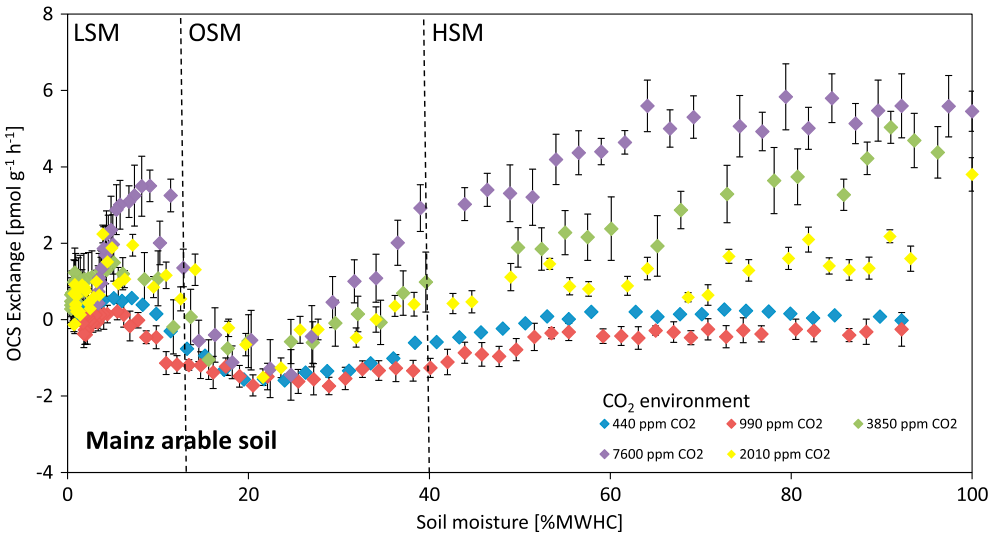

Figure 4. OCS exchange rates for the Mainz soil related to dry weight in pmol g^{-1} h^{-1} as a function of the soil moisture given as % MWHC. Negative exchange rates indicate OCS uptake. Dotted lines indicate the areas defined for the integration of exchange rates as given in Table 3. LSM, OSM, HSM = low, optimum, and high moisture range. Some error bars are smaller than individual points.

water content at the wetter point, J_{MWHCw} is the emission rate corresponding to $MWHC_w$, and J_{MWHCd} is the emission rate corresponding to $MWHC_d$. Accordingly, the total integrated OCS exchange for each soil moisture range is the sum of all trapezoids within its borders.

3. Results

3.1. Untreated Soils

Figure 4 demonstrates the exchange behavior of the soils as a function of the soil water content. Of the five untreated ("natural, nonsterilized," see experimental procedure) soils investigated, the exchange behavior of the four arable soils, exemplified in Figure 4 by the Mainz soil, depended strongly on soil moisture. Exchange rates for the other soils are shown in Figure S1 in the supporting information. In contrast to this general behavior, the "Suriname" rainforest soil showed more or less a constant emission, which decreased only at very low soil moisture (<2% MWHC).

Disregarding the Suriname soil, the other soil types exhibited a pattern of three distinguishable exchange rate ranges as a function of soil moisture, consisting of one range with an OCS uptake (or low OCS emission) and two ranges with an OCS emission, as indicated in Figure 4.

The exchange rates as integrated over the three defined ranges of soil moisture are shown in Figure 5. Within the low soil moisture range, OCS emission of the "Mainz," "Himalaya," and "Nördlingen corn" soils increased with rising CO_2 concentration. The "Nördlingen sugar beet" soil also shows OCS emission in this soil moisture range, but no change with increasing CO_2 concentration. Under optimal soil moisture conditions, a more general uptake behavior could be found. The trend of OCS exchange at optimal soil moisture was an uptake of OCS that was reduced and finally changed to an emission with rising ambient CO_2 mixing ratio for "Mainz," "Himalaya," and "Nördlingen corn" soil. In contrast, the trend for "Nördlingen sugar beet" was an increase of OCS uptake at optimal soil moisture with increasing CO_2 mixing ratio. The Himalaya soil exhibited an increase of the uptake with increasing CO_2 only up to 3850 ppm, followed by an emission under 7600 ppm CO_2. At high soil moisture, an emission was found almost exclusively for all soils with a strong increase at increasing CO_2 levels, except for the "Nördlingen sugar beet" soil. It is noteworthy to point out that the exchange rates (emission rates) at high soil moisture ranged an order of magnitude higher than at lower soil moistures.

3.2. Chloroform Fumigated Soils

Fumigation by chloroform significantly affected the OCS exchange at optimal soil moisture (Figure 6). OCS uptake by the "Mainz" soil increased strongly under higher CO_2 concentrations while at low

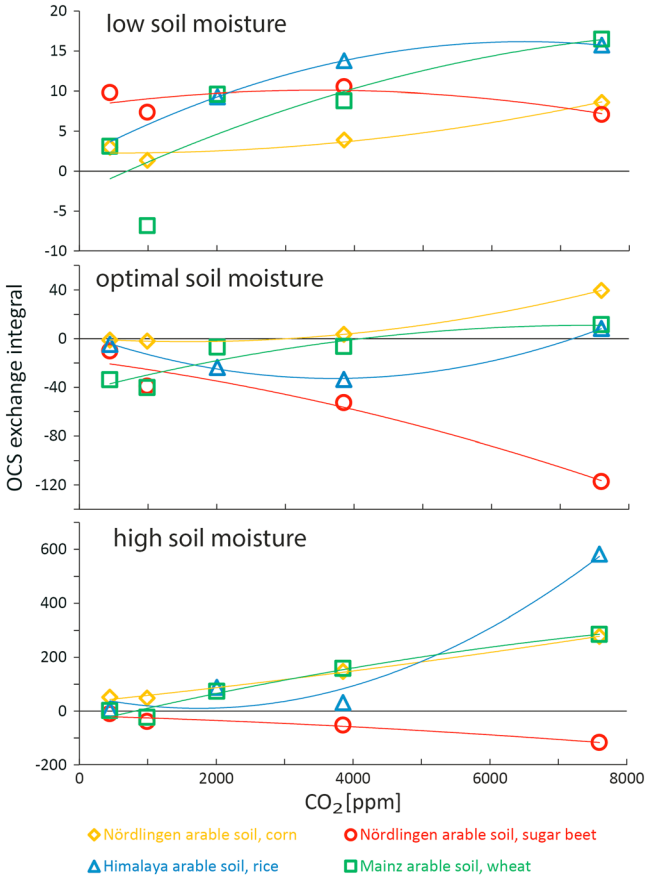

Figure 5. OCS exchange patterns for the four arable soils "Mainz," "Himalaya," "Nördlingen corn," and "Nördlingen sugar beet" at CO_2 mixing ratios from 442 to 7601 ppm. Exchange rates have been integrated for high, optimal, and low soil moisture. Negative values denote uptake, positive values emission of OCS.

concentrations uptake was reduced. It did not switch over to any emission. OCS exchange with "Nördlingen corn" soil switched over to an emission, dropped to an uptake at 4030 ppm, and then exhibited emission again at 7520 ppm, though only half of the amount was found without sterilization (see Figure 5). For "Nördlingen sugar beet" soil, which showed increasing uptake with increasing CO_2 only when untreated, an increase of the uptake at lower CO_2 and a reduction of the uptake at 7520 ppm were observed.

3.3. Treatment With Antifungal and Antibacterial Compounds

While chloroform acts more generally, treatment with antifungal and antibiotic compounds may allow a more specific interpretation. Therefore, we applied the agents nystatin (known as inhibitor of fungi) and streptomycin (known as inhibitor of bacteria, see section 2.4). We found only small differences between untreated and streptomycin treated samples. However, a significant shift toward emission was observed with nystatin (Figure 7) over the whole range of SWC conditions for the "Mainz" soil sample. The "Suriname" soil sample, exhibiting almost no variability related to SWC, showed a higher emission under nystatin and streptomycin treatment with strongest effects under nystatin.

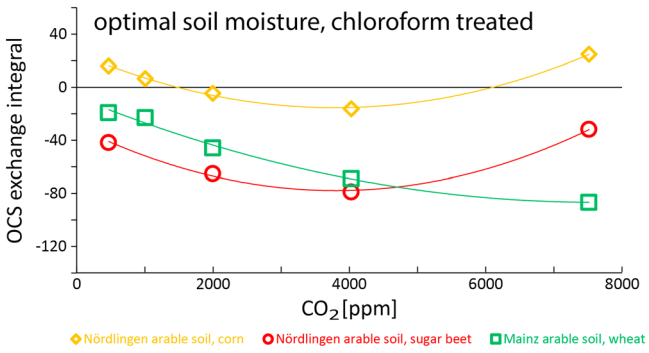

Figure 6. OCS exchange at different CO_2 concentrations after fumigation with chloroform vapor. Negative values denote uptake, positive values emission of OCS. All measurements were performed at optimal soil moisture.

4. Discussion

4.1. OCS Exchange as a Net Result of Consumption and Production

Biotic uptake and consumption [*Kesselmeier et al.*, 1999; *Protoschill-Krebs et al.*, 1996; *Seefeldt et al.*, 1995; *Lorimer and Pierce*, 1989], biotic production [*Jordan et al.*, 1997; *Jordan et al.*, 1995; *Katayama et al.*, 1992; *Smith and Kelly*, 1988], abiotic destruction [*Lehmann and Conrad*, 1996; *Elliott et al.*, 1989], and abiotic production [*Whelan and Rhew*, 2015; *Whelan et al.*, 2016; *Lehmann and Conrad*, 1996], have been reported either for mineral soils or for the

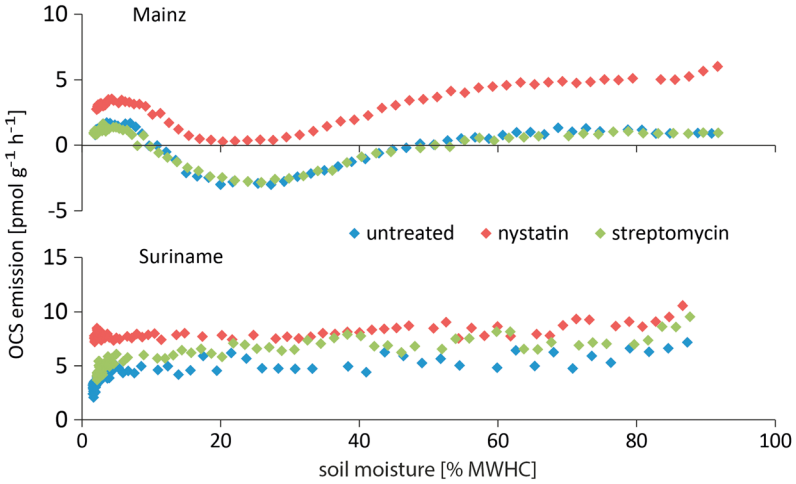

Figure 7. OCS exchange rate of untreated (blue diamonds), nystatin-treated (red diamonds), and streptomycin-treated (green diamonds) soil samples at 925 ppt OCS mixing ratio and 430 ppm CO_2 mixing ratio. Error bars are smaller than individual points.

organic fraction, including enzymes or organisms found in soils. Because the observed signal is a composite of the above-mentioned processes, which may differ among soil types and environmental conditions, all these sources and sinks must be considered in any net exchange observed.

4.2. OCS Exchange and Soil Moisture

Our results show a clear dependence of OCS exchange on soil moisture. OCS was released under high and very low soil moisture, whereas there was an uptake of OCS in an intermediate moisture range. There are two ways soil moisture can influence OCS exchange: microbial activity and diffusivity:

i Microbial activity: At different soil moistures, different microbial communities are active [*Drenovsky et al.*, 2004; *Cleveland et al.*, 2007; *Gleeson et al.*, 2010; *Oswald et al.*, 2013]. Depending on their enzymatic inventory, this may favor production or consumption.

ii Diffusivity: To be taken up by enzyme within a cell, OCS has first to reach those cells by diffusion. As a gas, OCS will reach its reaction site easier the lower the soil moisture becomes. At high soil moisture, much of the soil pore space is filled with water, impeding OCS diffusion. As the soil dries, diffusivity improves, allowing faster uptake. Such a dependence of OCS uptake on water-filled pore space has been shown by *Kesselmeier et al.* [1999] and *Van Diest and Kesselmeier* [2008]. Also, production and release is triggered by diffusivity, which influences oxygen availability. *Smith and Kelly* [1988] only saw OCS production under anaerobic conditions.

For all four arable soils, we observed an OCS exchange pattern with OCS emission at high soil moisture followed by OCS uptake at an optimal soil humidity and finally emission again at very low soil moisture. At high soil moisture, diffusivity is low (see (ii)), limiting OCS uptake. At the same time, enough water to dissolve thiocyanate is available, allowing the uptake of this precursor by microorganisms. Additionally, conditions are more anaerobic, which may be favorable to some OCS production pathways [*Smith and Kelly*, 1988].

When the soil moisture declines, reaching "optimal soil moisture," diffusivity and consequently OCS uptake improve (see (ii)). In parallel, conditions become more aerobic, worsening conditions for some OCS production pathways.

In addition, at different soil moistures, different microorganisms may be active (see (i)), possibly facilitating uptake or emission more strongly.

The final peak of OCS emission at very low soil moisture is harder to explain. Some authors report breakage of cells at very low soil water contents [*Ermel*, 2004], which may lead to release of trace gases. Such a process may be regarded as abiotic, but we cannot exclude this peak being caused by microorganisms adapted to this environment.

The available data do not allow to quantify the extent to which each of the mechanisms discussed above contributes to the observed net exchanges. However, we see no reason that would disqualify any of the above-discussed mechanisms. Also, most of them have been described in the literature previously (see section 4.1). It is reasonable to assume that all play a role to some extent. More studies, especially with different approaches, are highly desirable, and projects with isotopic and genetic techniques are already underway.

4.3. OCS Exchange Influenced by CO_2 Concentration

Increasing CO_2 up to normal soil levels as reported in the literature [*Hirano et al*., 2003; *Yonemura et al*., 2009; *Sakurai et al*., 2015] affected the observed OCS exchange patterns significantly. With increasing CO_2 at high soil water content, emission strongly increased under 7600 ppm CO_2. Even at optimal humidity, uptake was reduced under these conditions and in some cases changed to an emission, especially at the two highest CO_2 concentrations. Such a change in exchange behavior may be either due to increased production of OCS (i), decreased uptake (ii), or a combination of both.

i Increased CO_2 concentrations may boost the activity of OCS-producing bacteria. In culture studies, various authors observed increased growth and activity of microorganisms with increasing CO_2 [*Dehority*, 1971; *Repaske and Clayton*, 1978; *Samuelov et al*., 1991]. While *Repaske and Clayton* observed saturation at 400 ppm CO_2 for *Escherichia coli, Dehority* [1971] reported that many species and strains of bacteria needed a concentration of 1000 ppm atmospheric CO_2 for optimal growth; a few strains even required a 10% CO_2 atmosphere to reach maximal growth. In addition to an influence on the growth of *Anaerobiospirillum succiniciproducens, Samuelov et al.* [1991] found that increased levels of [CO_2/HCO_3^-] also induced to a shift between metabolic pathways with expression of different enzymes and accumulation of a different end product. Such a shift in the metabolic pathways could be the cause for the strong OCS emission increase at 7600 ppm CO_2 observed for some of our soils.

ii Enzymatic uptake of OCS may be competitively inhibited. Given the large concentration difference between OCS and CO_2 (1:10^6), CO_2 would have to occupy the binding site of all or nearly all enzyme molecules. An indicator for the substrate concentration at which this state is reached is the K_M value of an enzyme, which describes the substrate concentration at which half the maximal rate of turnover of an enzyme is attained. Beyond this concentration, the enzyme starts getting saturated, until more substrate will not increase conversion speed as all binding sites are occupied. Therefore, the CO_2 concentration in the soil water would have to exceed the K_M value of the enzyme in question. The K_M value of CA (and other enzymes) is not uniform throughout species and also depends on pH and temperature. The BRENDA database [*Schomburg et al.,* 2002; www.brenda-enzymes.org] offers K_M values for CA and CO_2 as substrate that, excluding macrofauna, macroflora. and marine algae, range from 0.089 to 80 m*M*. The reported values cluster in the range of 1–20 m*M*, with median value of about 17 m*M* (when averaging different entries for the same species). This fits rather well with the K_M values reported for bacterial CA by *Chirica et al.* [1997] (20 m*M*, CA typ A) and *Nishimori et al.* [2007] (14.7 m*M*, CA typ B). Only one entry in BRENDA is below 0.3 m*M* (or 5 out of 256 entries if none are omitted). *Ogée et al.* [2016] suggest a K_M value of about 3 m*M* as typical for CA in soils.

The equilibrium of CO_2 (or any other gas) between the gas phase and the liquid phase is described by Henry's' law. Henry's law takes many forms; one of them is $H^{cp} = c_a/p$ [*Sander*, 2015]. Here c_a is the CO_2 concentration in the aqueous phase in mol m^{-3}, p is the partial pressure of CO_2 in Pa, and H^{cp} is the Henry solubility in mol m^{-3} Pa^{-1}. *Sander* [2015] lists H^{cp} for CO_2 at 25°C and CO_2 as 3.3×10^{-4}. Corrected for 20°C by equation (19) in *Sander* [2015] H^{cp} (20°C) is 3.78×10^{-4}. Based on the Henry equilibrium and the CO_2 concentration in the gas phase, we calculated an approximation of the CO_2 concentration in the liquid phase. The calculated CO_2 in the pore water at a given atmospheric CO_2 mixing ratio is shown in Figure 8. Based on our calculated CO_2 concentration under the maximal gas phase concentration (7600 ppm), the K_M value of CA would have to be below 0.3 m*M* to cause a competition for the active center of the enzyme. As long as the CO_2 concentration in the aqueous phase is not notably above K_M value of CA, the rate of turnover will increase linearly with the increase of substrate concentration (in this case CO_2). This means that the enzyme is not saturated and some enzyme molecules still have free binding sites. All CO_2 concentrations in the aqueous phase were estimated to be well below the typical K_M value for CA and CO_2 and hardly any reported K_M value is below the

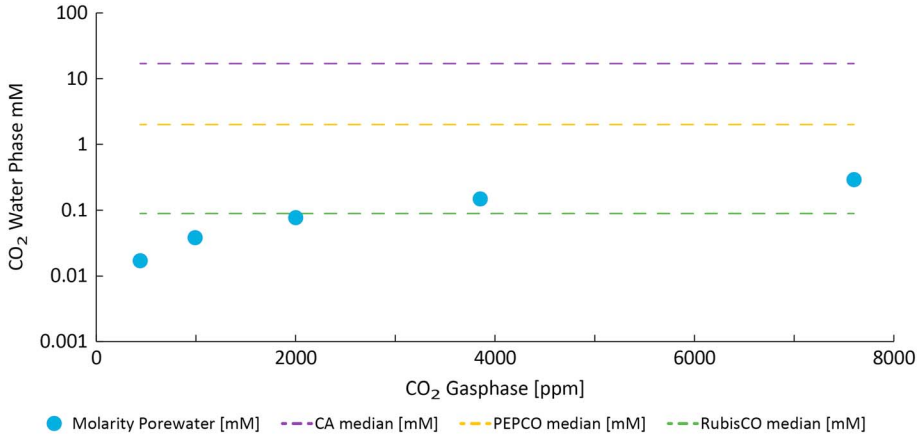

Figure 8. The K_M values of carbonic anhydrase (purple), PEPCO (yellow), and RubisCO (green) compared to the calculated CO_2 concentration in the water phase (blue dots). The expected water phase concentration was calculated from the known gas phase concentration following Henry's law. The K_M values are medians of data reported in the BRENDA database (see section 4.3).

highest CO_2 concentration we can expect for the aqueous phase. Therefore, we regard a competitive inhibition as highly unlikely. The same selection criteria were applied for PEPCO and RubisCO, yielding medians of 2 m*M* (range of 0.8–3.7 m*M*) and 0.09 m*M* (range 0.08–1.4 m*M*), respectively. *Badger and Bek* [2008] report a similar value for RubisCO (0.1 m*M*). Thus, inhibition of PEPCO is unlikely as well, but RubisCO might be affected at higher CO_2 concentrations (see Figure 8). It has been shown that soils can contain significant amounts of RubisCO [*Selesi et al*., 2007; *Videmšek et al*., 2009; *Salinero et al*., 2009; *KoilRaj et al*., 2012; *Nowak et al*., 2015; *Liu et al*., 2016]. If RubisCO is also contained in our samples, this inhibition would be part of the cause for the observed changes in OCS exchange at high CO_2 concentrations.

4.4. Chloroform Treatment Demonstrates Involvement of Biotic Processes

Fumigation by chloroform changed the exchange patterns and showed clear differences relative to untreated live soils. Despite the differences from soil to soil, some common trends were noticeable. Within the "optimal moisture range" (see Table 4), all three soils that were examined under chloroform sterilization showed a shift toward OCS uptake with rising CO_2 mixing ratios. When compared with their live counter parts, OCS uptake at high CO_2 mixing ratios (2010/2000 to 3850/4030 ppm) was boosted for all three soils, in case of the "Mainz" soil under up to 7600/7520 ppm CO_2. At lower mixing ratios (440/460 and 990/1010 ppm), uptake was reduced for "Mainz" and "Nördlingen sugar beet" and even switched to an emission (which declined with rising CO_2 mixing ratio) for "Nördlingen corn." At 7600/7520 ppm, CO_2 uptake of "Nördlingen sugar beet" and the emission of "Nördlingen corn" were lower than that of their live counterparts.

Since treatment with chloroform vapor only kills a portion of the bacteria and fungi in soils [*Ingham and Horton*, 1987] and both production and consumption of OCS might be impacted, a quantification of the biotic share of OCS exchange with this method is not possible. However, as the physical properties of the soil remain the same, the strong change in exchange behavior demonstrates the involvement of biotic processes. It is also possible that killing the microorganisms in a soil does not stop all biotic processes: *Maire et al.* [2013] reported that respiratory enzymes can survive outside of living cells within soils, establishing an extracellular metabolism (EXOMET). This may also be possible for enzymes such as CA (uptake of OCS) or carbon disulfide hydrolase (production of OCS) stabilized on soil particles in a similar fashion. The fact that chloroform acts by lysis of cell membranes [*Blankenship et al*., 2014] increases the possibility of enzymes leaving the dead cells and establishing such an EXOMET. Also, despite the cells being dead, enzymes involved in the exchange of OCS might become more accessible, after the elimination of the diffusion resistance through the cell membrane. The duration of this effect would be dependent on the time required to degrade such enzymes, but *Maire et al.* [2013] have shown that some respiratory enzymes can be stabilized on soil particles for days.

Despite some inconsistencies, there seems to be a trend of increased uptake of OCS after chloroform vapor treatment. In conjunction with *Ingham and Horton* [1987] reporting chloroform vapor to be less effective

against fungi than against other microorganisms [Table 6 in *Ingham and Horton*, 1987], this falls in line with other findings in this work which will be further discussed in section 4.6.

4.5. Special Exchange Behavior of Nördlingen Sugar Beet and Suriname Soil

i Suriname soil: The Suriname soil exhibited a more or less constant emission that decreased only at very low SWC. This behavior is not understood but was observed already earlier [*Van Diest*, 2007]. We found that this soil differed from all other soils in its organic content, carbon and nitrogen content, and pH (see Table 1). Interestingly, *Whelan et al.* [2016] also observed little variability in the OCS exchange of a rainforest soil when altering soil water content, while soils of other origins showed a strong reaction to changes in soil water content.

ii Nördlingen Sugar Beet soil: Compared to the other arable soils, the sugar beet soil showed an inverse reaction in OCS uptake to increasing CO_2 concentrations. Instead of a decrease of OCS uptake with increasing CO_2 concentration, we observed an increase for this soil. The abiotic properties of the sugar beet soil are rather similar to the other arable soils (see Table 1). The only prominent difference (especially to the other Nördlingen soil) is the fertilization practice. While the other three soils are conventionally managed, the sugar beet soil is organically fertilized. There is evidence that organically fertilized soil may contain more fungi than conventionally fertilized soil. *Anastasi et al.* [2005] found that both compost and vermicompost, typically applied for organic fertilization, contain very high amounts of fungi. This load of fungi was higher than or as high as the arable soils with the highest load reported by *Luppi Mosca et al.* [1976]. Applying such compost as fertilizer to a soil will consequently also transport fungi into the soil. In contrast, several authors describe a negative impact of conventional (mineral) fertilizer on mycorrhizal fungi [*Galvez et al*., 2001; *Oehl et al*., 2004; *Gryndler et al*., 2006]. *Gryndler et al.* [2006] also observed an increase of actinomycetes and arbuscular mycorrhizal fungi in organically fertilized soils, while the positive effect on saprotrophic fungi was not statistically significant. *Griffiths et al.* [1999] found that fungal biomass increased stronger than bacterial biomass when they loaded soil with organic carbon. *Birkhofer et al.* [2008] found that microbial biomass and activity of decomposer biota increased in comparison with soil that received only mineral fertilization, the effect being similar for bacterial and fungal biomass. *Wallenstein et al.* [2006] saw a decline of the fungal to bacterial activity ratio in forest soils that received mineral fertilization, and *DeForest et al.* [2004] saw a decrease of lignolytic enzyme activity in forest soil induced by mineral fertilization, indicating reduced activity by saprotrophic fungi. *Esperschütz et al.* [2007] found the highest fungal biomass in organically fertilized arable soils, when compared to conventionally or unfertilized arable soils. *Bittman et al.* [2005], however, observed a negative effect of organic fertilizing on hyphal length in grassland soils in comparison with unfertilized controls. This might be related to different land use type (grassland versus forest or arable soil). Thus, it is likely that the fungus to bacteria ratio within the "Nördlingen sugar beet" soil is higher than in the other arable soils, which were fertilized conventionally.

4.6. Fungi as Dominant OCS Consumers

Three trends in the presented measurements suggest that fungi are the dominant OCS consumers in the examined soils. (1) At optimal soil moisture, the one soil likely to have the highest fungi to bacteria ratio was the only one with a trend to stronger OCS uptake with increasing CO_2 (see section 4.5 (ii)). (2) After chloroform vapor treatment at higher CO_2 concentrations, we observed stronger uptake or less emission of OCS in comparison to live (untreated) soils. Following *Ingham and Horton* [1987], fungi populations will be less reduced than bacteria populations. We only know of reports of bacteria producing OCS [*Katayama et al*., 1992; *Smith and Kelly* [1988]; *Jordan et al*., 1995; *Jordan et al*., 1997; *Smeulders et al*., 2011] but are not aware of any reports of fungi producing OCS. If the producing populations (bacteria) are suppressed more intensely by chloroform than the main consumers (fungi), a shift toward net consumption is expected. This is observed mainly at high CO_2 and supports the idea that OCS production by bacteria is boosted by higher CO_2 concentrations (see section 4.3). The shift in the net exchange will be stronger at higher CO_2 concentrations because more OCS production than at low CO_2 concentrations will be taken away. (3) After antifungal treatment with nystatin, OCS emission was stronger than from the same soils after antibacterial or no treatment (see Figure 7). This may be regarded to result from an inhibition of fungi, resulting in a decrease of uptake. This view is supported by the absence of reports about fungi producing OCS.

5. Conclusions

For the majority of soils examined (four out of five), we found a correlation between OCS exchange and CO_2 concentration as well as between soil moisture and OCS exchange. All four arable soils showed a pattern going from OCS emission to uptake and finally to emission again when soils went from wet to dry state. The one soil ("Suriname") with no clear relation between OCS exchange, soil moisture, and CO_2 concentration was very different in pH, organic carbon content, soil structure, and sample age. This behavior may be typical for such kinds of soil.

Our results suggested that the net OCS exchange comprises biotic and abiotic processes. Fumigation with chloroform indicated that for the biotic component, OCS production exceeds consumption, especially at high soil moisture.

A comparison of estimated CO_2 concentrations in soil water with the K_M values of the enzymes involved in CO_2 and OCS uptake suggests that there is no competitive inhibition of PEPCO and CA at the CO_2 concentrations applied, whereas inhibition of RubisCO cannot be excluded.

The behavior of the organically fertilized "Nördlingen sugar beet" soil and preliminary experiments with selective sterilization agents suggested that fungi play a dominant role in biotic OCS uptake, as demonstrated for two completely different soil types, the arable "Mainz" and the tropical "Suriname" soils.

Our data demonstrate that soils may switch between acting as sinks or sources, which puts in question the use of the overall net exchange signal over an ecosystem as a GPP proxy. Accompanying soil exchange measurements must be included to check the significance of the soil exchange fluxes under the relevant field campaign conditions.

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