Diffusivity and enzymatic activity control the exchange of Carbonyl Sulfide (COS) between soils and the atmosphere

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Heidi Van Diest

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Zusammenfassung

Carbonylsulfid (COS) ist eines der stabilsten reduzierten schwefelhaltigen Spurengase in der Atmosphäre. In der gut durchmischten Troposphäre bewegt sich seine Konzentration um 500 ppt. COS spielt eine wichtige Rolle in der Produktion von stratosphärischem Aerosol und im Ozon Zyklus. Dieses Spurengas hat eine Vielfalt an natürlichen und anthropogenen Quellen, denen gleichstarke Senken, darunter die dominanten wie Vegetation und Boden, gegenüber stehen. Die Stärke der Senken ist trotz langjähriger Forschungen immer noch Gegenstand der Diskussionen. Daher ist es wichtig die kontrollierenden Parameter zu charakterisieren. Alle Austauschmessungen vor 1990 vermuteten Böden als Quelle von COS, was aber durch Castro and Galloway (1991) klar widerlegt wurde. Heute werden Böden in Ergänzung zur Vegetation grundsätzlich als Senke betrachtet.

Vor diesem Hintergrund wurden Bodenproben auf den Austausch von Carbonylsulfid mit der Atmosphäre unter verschiedenen Umgebungsbedingungen untersucht. Drei Ackerböden aus Deutschland, China und Finnland und zwei Waldböden aus Sibirien und Surinam konnten parametrisiert werden in Relation zur atmosphärischen Umgebungskonzentration, Temperatur und Bodenfeuchte (WC). Neben Umgebungskonzentration und Bodenfeuchte, scheinen Bodenstruktur und enzymatische Aktivität die Richtung und Größe des Austauschflusses zu kontrollieren. Die übereinstimmenden Optima für boreale Böden in Relation zum wassergefüllten Porenvolumen des Bodens (WFPS) und die Linearität zwischen Depositionsgeschwindigkeit (V_d) und Bulk density lassen auf eine Dominanz der Abhängigkeit der COS-Aufnahme von der durch WFPS bestimmten Diffusionsfähigkeit schließen. WFPS ist abhängig von WC, Bodenstruktur und Bodenporosität. In Ergänzung zu diesen eher physikalischen Parametern konnte die Carboanhydrase (CA) als kontrollierendes Enzym in Böden identifiziert werden. Erste Versuche zur direkten Bestimmung der CA in den untersuchten Böden erlaubten eine erste, aber noch sehr ungenaue Abschätzung der Enzymaktivität.

Carpe Diem!

Voor mijn ouders:
Dank u!

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1. Introduction

Life on earth is inextricably linked to climate through a variety of interacting cycles and feedback loops. In recent years there has been a growing awareness of the extent to which human activities, such as deforestation and biomass burning, have directly or indirectly modified the biogeochemical and physical processes involved in determining our climate. One way that climate influences life is by regulating the flow of substances through these biogeochemical cycles.

1.1. Biosphere exchanges: Biogeochemical cycle of sulfur

In biogeochemistry, the sulfur cycle is one of the most complex cycles because oxidation of sulfur varies between –2 and +6. Furthermore, the sulfur cycle has a large variety of organic and inorganic species (Figure 1.1). Sulfur as an essential nutrient for living species can be found everywhere in the environment. In its reduced oxidation state, sulfur plays an important role in the structure and function of proteins. In its fully oxidized state, sulfur exists as sulfate and is the major cause of acidity, which makes sulfur important to geochemical, atmospheric, and biological processes such as the natural weathering of rocks, acid precipitation, and rates of denitrification.

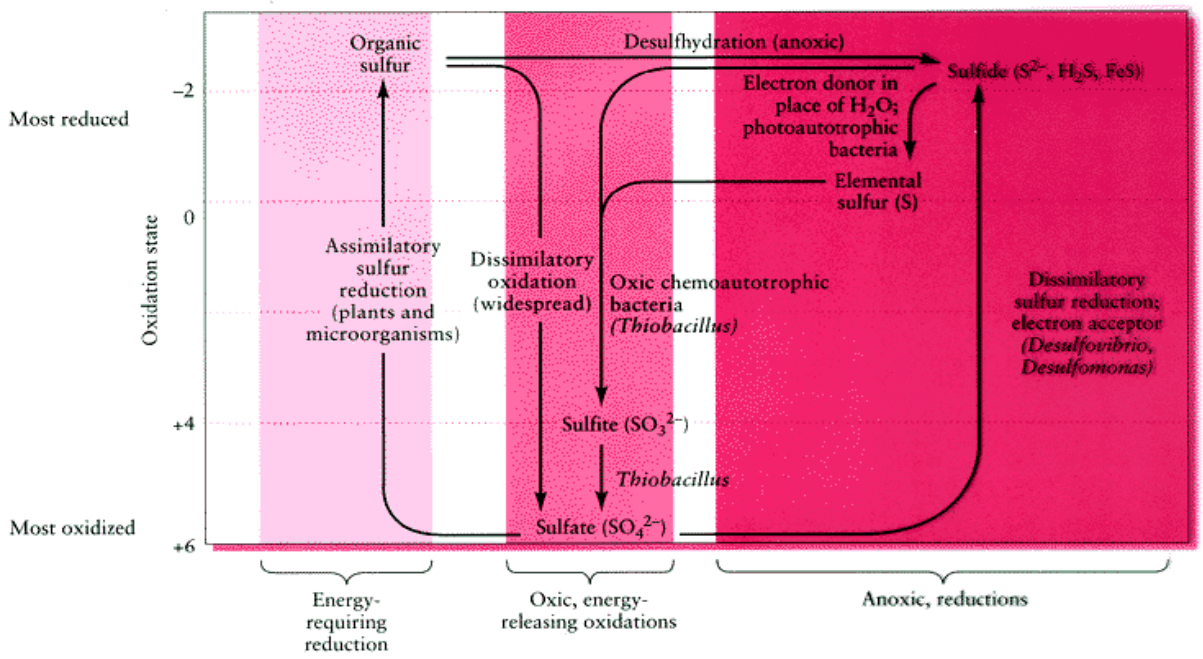

Figure 1.1: Oxidation of sulfur varies between -2 and +6 with a large variety of organic and inorganic species (edited from California State University, Monterey Bay, Sulfur Cycle).

Unfortunately, large uncertainties remain concerning the chemical species and the magnitude of natural emission of sulfur gases into the atmosphere. Anthropogenic sources mainly emit sulfur dioxide (SO_2) which is oxidized to sulfate (SO_4^{2-}). Biogenic sources emit substantial amounts of other sulfur (S) species (Figure 1.2), which are summarized as reduced volatile sulfur compounds, such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), carbonyl sulfide (COS), carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3; DMS) and dimethyl disulfide (CH_3SSCH_3; DMDS) (Yang *et al.*, 1996; Kesselmeier, 2005). Lefohn *et al.* (1999) give a good description of the sources and the contribution of anthropogenic sulfur gases in the atmosphere. Lefohn *et al.* (1999) also developed a database of annual estimates of national sulfur emissions from 1850 to 1990, based on net production, sulfur content and sulfur release factors for each country´s production activities (Lefohn *et al.*, 1999).

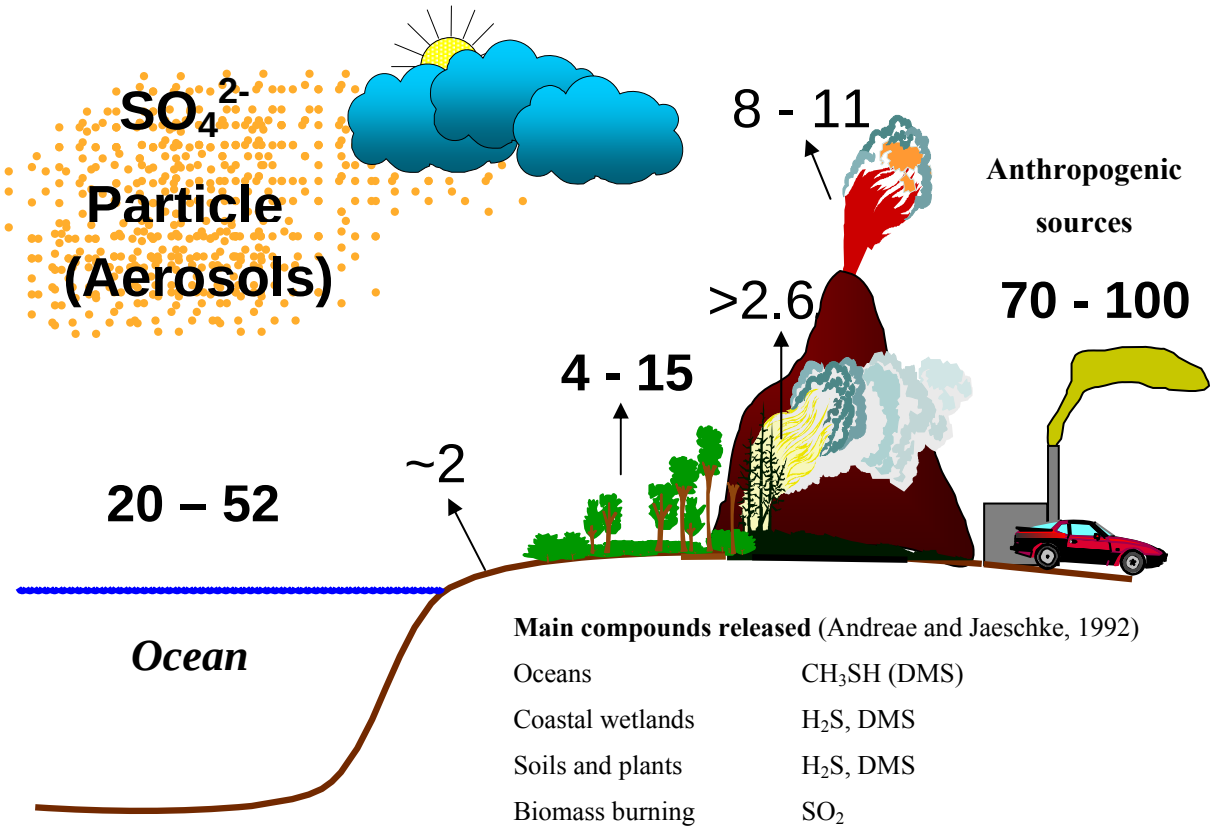

Figure 1.2: Estimated ranges of global emissions of volatile sulfur compounds (Tg a^{-1}) (Kesselmeier, 2005).

1.2. The importance of Carbonyl Sulfide (COS) in the atmosphere

Among all sulfur trace gases, carbonyl sulfide (COS) is recognized as one of the most abundant volatile sulfur compounds in the atmosphere with an average global concentration of approximately 500 ppt (Barnes *et al.*, 1994; Kjellström, 1998). Estimates suggest a tropospheric lifetime of COS of about 2 to 7 years (Khalil and Rasmussen, 1984; Barnes *et al.*, 1994; Chin and Davis, 1995; Cutter *et al.*, 2004), because it is nearly inert to photochemical decomposition in the troposphere, as a consequence, most of it is transported into the stratosphere where it undergoes photodissociation as well as oxidation with O (^{3}P) atoms and OH radicals (Crutzen, 1976; Chin and Davis, 1995). The reaction products are eventually oxidized to H_2SO_4, which then condenses to form aerosol particles (Figure 1.3).

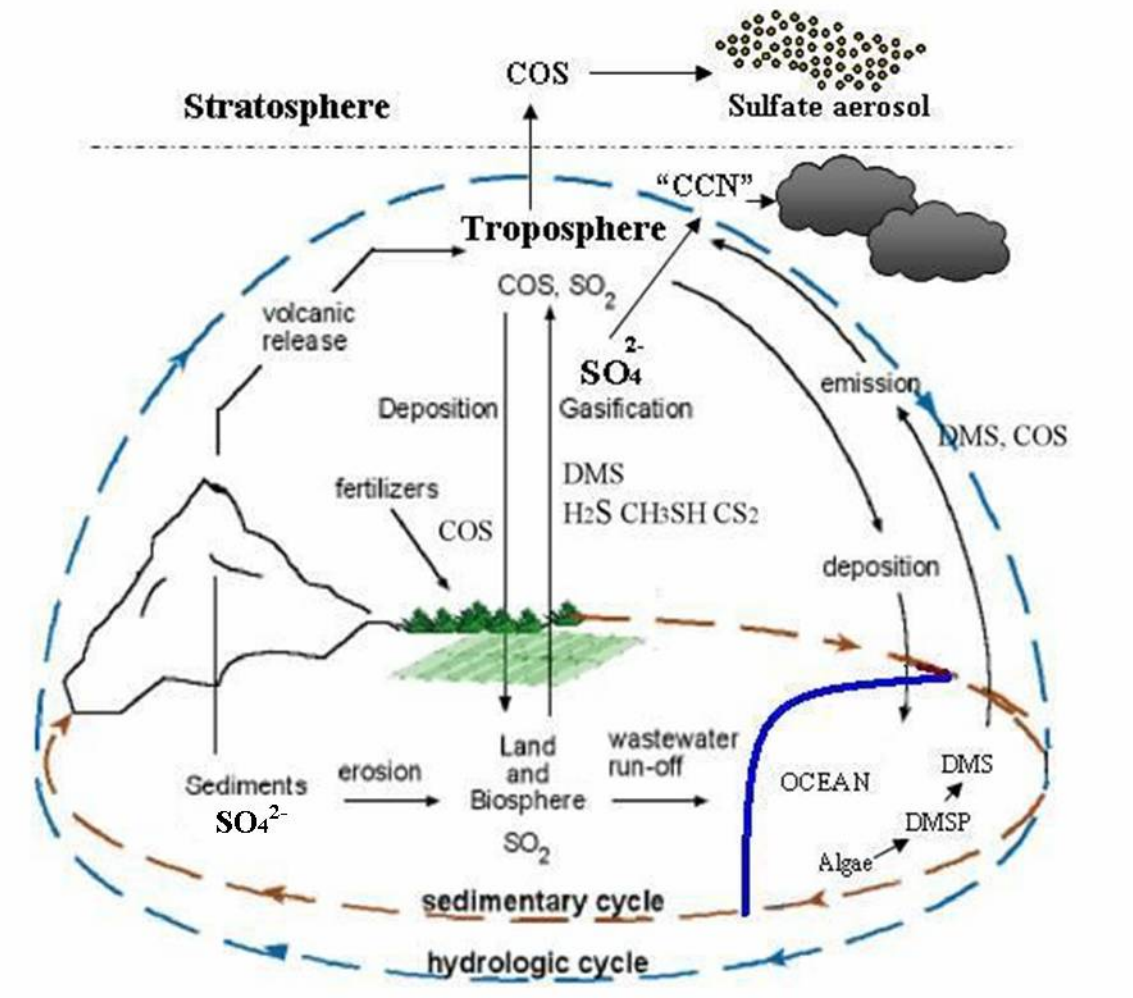

Figure 1.3: The biogeochemical sulfur cycle and the role of carbonyl sulfide in the atmosphere (edited from Carnegie Mellon University, Sulfur Cycle).

The role of atmospheric COS in the stratospheric aerosol layer was first studied by Crutzen (1976). Even during extended periods of little or no volcanic activity, there is a persisting layer of aerosol particles near 18 – 20 km, mainly consisting of a mixture of sulfuric acid and water. The continued existence of the stratospheric sulfate layer even under such conditions is normally explained by diffusion of tropospheric SO_2 into the stratosphere, where SO_2 is oxidized to H_2SO_4. Also H_2S and $(CH_3)_2S$ have been proposed to play a major role. Although it seems impossible that sufficient quantities of these gases can reach the stratosphere due to their short lifetimes of only 2.7 days (Friend, 1973). Crutzen (1976) estimated that the flux of COS to the stratosphere contributes about 0.1 % of the total industrial input of SO_2 into the atmosphere. The COS cycle seems to contribute only in a minor fraction of the sulfur cycle, nevertheless, it could be significant for the stratosphere.

The aerosol layer ("Junge" layer) plays an important regulatory role in the Earth's radiation balance (Ko, 2003) and has a consequent influence on climate (Turco *et al.*, 1980). The idea has been supported by early models (Turco *et al.*, 1980), but has been challenged by more recent model results such as from Kjellström (1998). Hoffmann (1990) has observed a long-term trend in the stratospheric aerosol level and speculated that increased COS levels could be responsible (Hofmann, 1990).

Although, Montzka *et al.* (2004) measured COS and other trace gases in Antarctic firn air and air trapped in ice and provided evidence for substantial declines during recent years in the Southern hemispherical atmosphere. These atmospheric decreases coincide with declines in global anthropogenic sulfur emissions of 15 – 20% noted by others over this period. The atmospheric history derived from the firn and ice data also suggests substantially lower atmospheric mixing ratios of COS during preindustrial times, which are 34 – 43% lower than observed in modern time. Surprisingly, this difference is larger than expected when the estimated contribution of anthropogenic emissions to total COS emissions is considered. This apparent discrepancy may reflect the large uncertainties in estimates of COS sources, or even may suggest substantial changes in non-anthropogenic fluxes over the past 150 years (Montzka *et al.*, 2004). Although, the atmospheric histories inferred for COS over Antarctia during this period closely follow global anthropogenic sulfur emissions (Stern, 2005).

The mixing ratio of COS is nearly constant throughout the entire troposphere at approximately 500 ppt and has therefore almost no vertical gradient. In the stratosphere the

COS mixing ratio is found to decrease rapidly with altitude, decreasing from near 500 ppt at the tropopause to less than 10 ppt at about 30 km (Chin and Davis, 1995). In contrast, latitudinal gradients in COS in the troposphere have been reported by several investigators (Deutscher *et al.*, 2006). Johnson *et al.* (1993) reported a latitudinal gradient of COS with an increase of between 1.6 and 2 ppt per degree of latitude in the northerly direction (Johnson *et al.*, 1993). In recent works ratios for the northern to southern hemisphere have been calculated to be 1.14 ± 0.06 (Rinsland *et al.*, 1992; Griffith *et al.*, 1998; Rinsland *et al.*, 2002), 1.25 (Bingemer *et al.*, 1990), 1.09 ± 0.07 (Sturges *et al.*, 2001) and 1.05 (Weiss *et al.*, 1995b; Thornton *et al.*, 1996). This indicates a larger abundance of COS in the northern hemisphere.

1.3. Global budget: sources and sinks

According to Watts (2000) and Kettle *et al.* (2002) total global sources and sinks are now balanced within the uncertainties of the estimates. The total source strength into the atmosphere was estimated to be 1.31 ± 0.25 Tg a^{-1} (Watts, 2000).

Known sources of COS are from both natural sources such as oceans (Ferek and Andreae, 1984; Johnson and Harrison, 1986; Mihalopoulos *et al.*, 1992), volcanism (Cadle, 1980; Khalil and Rasmussen, 1984; Belviso *et al.*, 1986), precipitation (Belviso *et al.*, 1987; Mu *et al.*, 2004) and marshes (Aneja *et al.*, 1979; Steudler and Peterson, 1984) as well as from anthropogenic sources as biomass burning (Crutzen *et al.*, 1985), coal-fired power plants, sulfur recovery and chemical processing (Khalil and Rasmussen, 1984).

The largest anthropogenic source of COS is believed to be atmospheric oxidation of industrially produced CS_2 (Bandy *et al.*, 1993), which is derived primarily from the manufacture of viscose rayon (Watts, 2000; Sturges *et al.*, 2001). Laboratory studies have found that the CS_2 to COS product ratio is unity so that for each CS_2 molecule emitted into the atmosphere, a molecule of COS will be produced (Johnson and Bates, 1993). COS is one of the trace gases produced from incomplete biomass burning during the smoldering stage. The production is typically reported as the volume mixing ratio of COS to CO_2 and estimated at 0.14 Tg a^{-1}. The COS amount produced from coal combustion from power plants can be estimated from the CO_2 released from the same source (0.036 Tg a^{-1}). Watts (2000) suggested that anthropogenic sources account for 26 ± 12% of all sources.

An indirect source is dimethyl sulfide (DMS) which is mostly emitted by oceans and is oxidized in the atmosphere (Khalil and Rasmussen, 1984; Becker *et al.*, 1990; Barnes *et al.*, 1994). More recent work (Yvon-Lewis and Butler, 2002) concerning oceanic loss rates for COS, suggests that the gross ocean-to-atmosphere flux for COS is over 2 times as large as the net oceanic flux of 0.3 Tg a^{-1} considered by Watts (2000).

Sinks are primarily thought to be vegetation (Brown and Bell, 1986; Goldan *et al.*, 1988; Sandoval-Soto *et al.*, 2005) and soils (Chin and Davis, 1993; Kesselmeier *et al.*, 1999) for this trace gas. Photolysis and reactions with O and OH radicals in the stratosphere are also important loss processes for COS. The global annual sink strength mentioned above was estimated to be 1.66 ± 0.79 Tg a^{-1} (Watts, 2000).

There are a number of chemical reactions which remove COS in the stratosphere (Crutzen, 1976; Khalil and Rasmussen, 1984; Chin and Davis, 1993; Chin and Davis, 1995):

(R1) The photodissociation of COS is far the most important among these processes

$$COS + h\nu \rightarrow CO + S$$

This photochemical process requires radiation having a wavelength of 388 nm or shorter.

(R2) Photo-oxidation: $COS + O(^3P) \rightarrow CO + SO$

(R3) $COS + OH \rightarrow CO_2 + HS$

The reaction products of those chemical reactions S, SO and HS are eventually oxidized to H_2SO_4. The reaction rates for these processes (R1, R2, R3) in the troposphere are extremely slow, resulting in a COS mixing ratio that is nearly constant throughout the troposphere. In the stratosphere, in conjunction with reduced vertical mixing, these processes lead to a significant vertical gradient in the COS profile (Chin and Davis, 1995).

1.3.1. Overview

Since COS in an important trace gas in the atmosphere and is suggested to play an important role in the stratospheric aerosol layer, the understanding and quantification of its sources, sinks, lifetimes, and global budget are of considerable scientific interest.

The following sources of COS are identified:

- ✓ Oceans;
- ✓ Soils and marches;
- ✓ Volcanoes;
- ✓ Biomass burning;
- ✓ Anthropogenic sources as coal combustion, sulfur recovery, cars and aluminum production;
- ✓ CS_2 conversion and precipitation.

Table 1.1 gives an overview of estimates of sources found in literature.

Table 1.1: Estimates of sources of carbonyl sulfide found in literature

Sources	***[Tg (COS) a^{-1}]***	***Literature***
Oceans	0.6 ± 0.3	(Rasmussen *et al.*, 1982)
	0.87	(Ferek and Andreae, 1984)
	0.2 – 0.4	(Johnson and Harrison, 1986)
	0.64	(Andreae, 1985; Andreae, 1986)
	0.32 (0.16 – 0.64)	(Chin and Davis, 1993)
	0.30 ± 0.18	(Watts, 2000)
	0.056	(von Hobe *et al.*, 2001)
Open oceans	0.10 ± 0.15	(Watts, 2000)
Coastal seas	0.30 – 0.60	(Mihalopoulos *et al.*, 1991)
	0.47	(Andreae and Ferek, 1992)
	0.06	(Ulshöfer *et al.*, 1996)
Indirect source		
DMS oxidation	0.10 – 0.28	(Barnes *et al.*, 1994)
Soils and Marshes	0.02 (0.01 – 0.06)	(Khalil and Rasmussen, 1984)
	0.27 (0.14 – 0.52)	(Chin and Davis, 1993)
	0.02 ± 0.01	(Watts, 2000)

Volcanoes	0.02	(Cadle, 1980)
	0.02 (0.01 – 0.05)	(Khalil and Rasmussen, 1984)
	0.006 – 0.09	(Belviso *et al.*, 1986)
	0.02 (0.006 – 0.09)	(Chin and Davis, 1993)
Biomass Burning	0.2 (0.1 – 0.5)	(Khalil and Rasmussen, 1984)
	0.11	(Kelly and Smith, 1990)
	0.14 ± 0.12	(Chin and Davis, 1993)
	0.07 ± 0.05	(Nguyen *et al.*, 1995)
Anthropogenic		
Coal combustion	0.036 ± 0.011	(Chin and Davis, 1993)
Sulfur recovery	0.002 (0.001 – 0.004)	(Chin and Davis, 1993)
Cars	0.06	(Peyton *et al.*, 1976)
	0.0008 – 0.008	(Fried *et al.*, 1992)
	0.04 ± 0.02	(Chin and Davis, 1993)
	0.006 ± 0.004	(Watts and Roberts, 1999)
Aluminum production	0.08 ± 0.06	(Harnisch *et al.*, 1992)
Total	0.124 ± 0.061	(Watts, 2000)
CS_2 conversion	0.6 (0 – 2)	(Khalil and Rasmussen, 1984)
	0.81 ± 0.06	(Chin, 1992)
	0.39 ± 0.29	(Chin and Davis, 1993)
	0.42 ± 0.12	(Watts, 2000)
Precipitation	0.13 ± 0.06	(Watts, 2000)
Total source strength	2	(Khalil and Rasmussen, 1984)
	1.23 (0.83 – 1.71)	(Chin and Davis, 1993)
	1.31 ± 0.25	(Watts, 2000)

The sinks of COS are thought to be:

- ✓ Vegetation;
- ✓ Soils;
- ✓ Reaction with OH, reaction with O and photolysis.

Table 1.2 gives an overview of sinks found in literature.

Table 1.2: Estimates of sinks of carbonyl sulfide found in literature

Sinks	***[Tg (COS) a^{-1}]***	***Literature***
Vegetation	2 – 5	(Brown and Bell, 1986)
	0.24 – 0.59	(Goldan *et al.*, 1988)
	0.53 ± 0.40	(Chin and Davis, 1993)
	1 – 3.4	(Hoffman, 1993)
	0.93 ± 0.07	(Kesselmeier and Merk, 1993)
	0.63	(Schlesinger, 1996)
	2.3 ± 0.5	Matthews, 1997
	0.56 ± 0.10	(Watts, 2000)
	0.2 – 1	(Kettle *et al.*, 2002)
	0.5 – 2.8	(Xu *et al.*, 2002)
	1.4 – 2.8	(Sandoval-Soto *et al.*, 2005)
Coniferous forest	0.04 ± 0.008	Estimated from (Kindermann *et al.*, 1995a; Kindermann *et al.*, 1995b; Kuhn *et al.*, 1999)
Temperate forest	0.05 ± 0.01	(Kuhn *et al.*, 1999)
Soils	0.04	(Brown and Bell, 1986)
	0.33 ± 0.19	(Chin and Davis, 1993)
	0.92 ± 0.85	(Watts, 2000)
Reaction with OH	0.13 ± 0.10	(Chin and Davis, 1993)
Reaction with O	0.02 ± 0.01	(Chin and Davis, 1993)
Photolysis	0.03 ± 0.01	(Chin and Davis, 1993)
Total sink strength	0.79 (0.30 – 1.52)	(Chin and Davis, 1993)
	1.66 ± 0.79	(Watts, 2000)

Chin and Davis (1993) reported that the global atmospheric COS budget seems to have either an overestimation of sources, or an underestimation of sinks, of approximately 30 %.

According to Watts (2000), total global sources and sinks are estimated as 1.31 ± 0.25 Tg a^{-1} and 1.66 ± 0.79 Tg a^{-1}, respectively. This budget seems to be balanced within the uncertainties of the estimates. However, recent estimates by Xu *et al.* (2002) and Sandoval-Soto *et al.* (2005) demonstrate vegetation as a bigger sink for COS as previously thought. This suggests the COS budget as unbalanced again. The uptake of COS by various biomes appears to be complicated and dependent on moisture, temperature, light intensity and microbial activity (Thornton *et al.*, 1996). Also soils seem to act rather as a sink than as a source. This indicates an urgent need for more data about the exchange capability of COS between soils and the atmosphere; therefore, in this work we concentrated our investigations on the uptake of COS by different soil types around the world.

1.3.2. Atmosphere – ocean

The ocean is believed to be a source of COS since its observed concentrations in open oceans are almost always supersaturated (Andreae, 1985; Andreae, 1986).

Oceanic COS concentrations are the result of a number of processes:

(i) Photochemical production from dissolved organo-sulfur species (Zepp and Andreae, 1994);
(ii) Non-photochemical production from dissolved organo-sulfur species or sediments (Flock and Andreae, 1996);
(iii) Hydrolysis of dissolved COS (Radford-Knoery and Cutter, 1994);
(iv) Air – sea exchanges (Radford-Knoery and Cutter, 1994).

In early work, Ferek and Andreae (1984) suggested that COS was produced in the ocean by the photochemical oxidation of sulfur-containing dissolved organic matter (DOM) and dissolved amino-acids (Zepp and Andreae, 1994). A study by Zepp and Andreae indicated that COS is formed by the photosensitized oxidation of organosulfur compounds that do not directly absorb sunlight.

Chin and Davis (1993) estimated a two times lower COS flux from the ocean to the atmosphere in comparison with Andreae (1985, 1986). Andreae didn't take seasonal variations into considerations. However, it is well established that COS production is highly light intensity dependent. Therefore, COS produced in seawater during summer periods is

expected to be higher than in winter times (Chin and Davis, 1993). Moreover, supersaturation ratio in the coastal and shelf water observed by Andreae (1986) is much higher than reported for other coastal waters, which is therefore not representative for the coastal waters on a global scale. Nevertheless, Weiss *et al.* (1995a) have reported that COS photoproduction rates are up to an order of magnitude larger in coastal water compared with the open ocean. In contrast, Weiss *et al.* (1995b) first reported the discovery of extensive regions of undersaturation, and therefore argue an overestimation of the previous reported global ocean fluxes. These results also indicate that the open ocean acts as a weak sink to atmospheric COS.

In addition to the seasonal and regional variations in COS saturation rates (SRs), the SRs also exhibit a strong diurnal variation. The observations of the 2- to 4-hour time lag by Andreae and Ferek (1992) between the maximum light intensity and maximum COS concentrations were consistent with the observations of Weiss *et al.* (1995b).

Light and wind speed seem to be the main determinants of the flux of COS from the oceans into the atmosphere (Weiss *et al.*, 1995b). Mu *et al.* (2004) measured the concentration of initial dissolved COS and its photochemical production rates by natural sunlight in precipitation samples (rain and snow). Unexpected high amount of COS was produced under natural sunlight irradiation. Earlier studies (Zepp and Andreae, 1994; Weiss *et al.*, 1995a) already indicated that the wavelength between 310 nm and 370 nm was largely responsible for COS photochemical production in seawater.

It is noteworthy that the available observational data (both open and coastal ocean) all show maximal COS production during the summer/autumn periods, when light levels and DOM and dissolved amino acids are maximal.

1.3.3. Atmosphere – vegetation

The role of vegetation as a major global tropospheric sink for COS has been studied for almost 25 years and is undisputed. It was first observed by Taylor *et al.* (1983) and Kluczewski *et al.* (1983, 1985), but the uncertainty in the quantitative estimates of this sink is still large (Kluczewski *et al.*, 1983; Tayler *et al.*, 1983; Kluczewski *et al.*, 1985; Brown and Bell, 1986; Fall *et al.*, 1988; Goldan *et al.*, 1988; Hoffman *et al.*, 1992; Kesselmeier *et al.*, 1993; Kesselmeier and Merk, 1993; Huber, 1994; Kuhn, 1997; Kuhn and Kesselmeier, 2000;

Xu *et al.*, 2002; Geng and Mu, 2004; Geng and Mu, 2005; Sandoval-Soto *et al.*, 2005; Geng and Mu, 2006). Xu *et al.* (2002) measured the fluxes of COS over a spruce forest in Central Germany and observed deposition velocities (V_d; relative to the leaf area) for COS which averaged at 1.1 ± 0.7 mm s^{-1}. This agrees well with V_d obtained in other laboratory and in situ studies (Tayler *et al.*, 1983; Kluczewski *et al.*, 1985; Goldan *et al.*, 1988; Kesselmeier and Merk, 1993; Huber, 1994; Kuhn, 1997), although quite different plant species were investigated in most of these studies.

Two common methods to estimate the global COS sink strength of vegetation were reported. Brown and Bell (1986) estimated the sink strength based on the ambient concentration and the deposition velocity. Goldan *et al.* (1988) suggested that vegetation accounts at least for 50 % of the net global loss of COS from the troposphere. Hoffman *et al.* (1992) and Chin and Davis (1993) assumed that the deposition velocity of COS and CO_2 are the same and they therefore used the correlation between the deposition velocity and the CO_2 assimilation.
Brown and Bell (1986) already hypothesized that COS is assimilated by a common mechanism; namely the hydrolysis to CO_2 and H_2S through the catalysis with the enzyme carbonic anhydrase (CA). CA is now recognized as the key enzyme for the uptake of COS in higher plants (Protoschill-Krebs *et al.*, 1995; Protoschill-Krebs *et al.*, 1996; Blezinger *et al.*, 2000; Haritos and Dojchinov, 2005). This enzyme explains the close relationship between CO_2 exchange and COS uptake found. Recent models (Schenk *et al.*, 2004; Yonemura *et al.*, 2005; Notni *et al.*, 2007) also confirm CA as one of the key enzyme for the uptake of COS. This assumption is also supported by the optimum curve resulting from plotting the COS uptake against respiration rates. But the uptake of COS seems to be inhibited at higher CO_2 respiration values because of the competition with CO_2 on the enzymatic level (Kesselmeier and Hubert, 2002). This indicated that COS deposition velocity in daytime was closely related to photosynthesis. In addition, temperature seems to play an important role. An enzyme increases its turnover with increasing temperature, but this trend is superimposed by a decrease of activity if the temperature range exceeds a certain value owing to reorganization and/or denaturation of the enzyme structures (Kesselmeier *et al.*, 1999). Temperature also plays an important role on regulating leaf stomata, via which plants take up COS.

Kuhn *et al.* (1999) assumed that the uptake of COS by higher plants was completely under stomatal control and considered the COS exchange of higher vegetation during nighttime to be negligible. However, the lawn, investigated by Geng and Mu (2004) had larger COS

deposition velocities at night, this implied that a light-independent process might exist for the grasses. Although, Protoschill-Krebs *et al.* (1996) pointed out that carbonic anhydrase (CA) was a light-independent enzyme and CA-induced uptake of COS might occur independently from light.

In recent studies, Sandoval-Soto *et al.* (2005) investigated the close correlation between the rate of photosynthesis and the COS uptake for different European tree species and considered the differences in deposition velocities for CO_2 and COS. Based on the Net Primary Production (NPP) global estimates of COS as a sink for vegetation were improved. The COS uptake closely followed the light/dark cycle, nevertheless low uptake rates were still reported under dark conditions. This could be explained by the incomplete closure of the stomata during night. Although, the close relationship between light and COS uptake in contrast to the light independent consumption by the catalytic enzyme CA supports the hypothesis of an exclusively stomatal uptake pathway. The final proof was given by the treatment with the synthetic plant hormone abscisic acid (ABA), which triggers the closure of stomata in plants. After infiltration of ABA a fast decline of CO_2 exchange down to zero and a decrease of COS uptake was observed. Sandoval-Soto *et al.* (2005) concluded that the prompt decline of assimilation to a zero-exchange of CO_2 under light conditions is a most convincing argument for the strict regulation of this trace gas exchange by stomatal aperture.
They also argue that a compensation point or the relationship between the uptake and atmospheric concentration will interfere with their estimates. Moreover, Sandoval-Soto *et al.* (2005) incorporated the deposition velocities of COS and CO_2 instead of their uptake ratios, hereby the linear relationship between the exchange of COS and its atmospheric concentration is already considered. The close relation of COS uptake to photosynthesis and the clear consumption pathway via stomatal uptake allowed a recalculation of the COS uptake by terrestrial vegetation. It could be necessary to take the deposition velocities for the uptake of COS in relation to CO_2 into account when estimating a COS sink strength from NPP. This leads to a significant increase of the COS sink strength estimate for terrestrial vegetation in the range of 1.4 – 2.8 Tg a^{-1}. Earlier estimates did not take this into account and may therefore be regarded as too low.

This result questions the balance of known sinks and sources. Therefore, it is important to re-investigate all COS sinks and sources (Sandoval-Soto *et al.*, 2005).

1.3.4. Atmosphere – soil

During the last decades several investigations have revealed that soils are involved in the atmospheric sulfur cycle.

All of the soil-atmosphere exchange measurements done before 1990 presumed that soils account for approximately 25% of the total source strength of COS (Andreae and Jaeschke, 1992; Chin and Davis, 1993). However these estimates are based on soil studies using enclosure methods with COS-free sweep air. This generates an artificial COS concentration gradient, which enhances the diffusion of COS from the soil to the atmosphere. Furthermore, this could lead to an overestimation of the natural emission strength. Therefore, field experiments under ambient concentrations of COS in the nineties gave convincing evidence that soils act more as a sink than as a source for COS (Castro and Galloway, 1991; Kesselmeier *et al.*, 1999; Kuhn *et al.*, 1999; Geng and Mu, 2004; Steinbacher *et al.*, 2004). Taking soils into account as COS sinks lead to an obviously more balanced global budget of sinks and sources (Andreae and Crutzen, 1997). Further work suggested that inappropriate use of air mixtures for flushing enclosures could mask possible uptake capability of COS by soils. It is meanwhile well accepted that the level of ambient trace gas concentration has a major control over the direction as well as the magnitude of the trace gas flux between biosphere and atmosphere (Castro and Galloway, 1991; Kesselmeier *et al.*, 1993; Kesselmeier and Merk, 1993; Lehmann and Conrad, 1996; Simmons *et al.*, 1999; Conrad and Meuser, 2000). Therefore, for a better understanding of the role of soils as an important sink for COS, Kesselmeier *et al.* (1999) have investigated this uptake under controlled laboratory conditions.

The soil biota's are active throughout the year and are independent on the light regime. Therefore, soils are able to take up COS continuously, but are still subject to dial or seasonal limitations caused by temperature and soil water content effects. Some important field measurements were carried out by Steinbacher *et al.* (2004). They investigated the exchange of COS between the atmosphere and soils in a temperate zone spruce forest in Germany. All measurements showed a net COS flux from the atmosphere into the soil. The average uptake of COS between the three campaigns was 0.81 ± 0.03 pmol m^{-2} s^{-1} and the total range was between 0.23 and 1.38 pmol m^{-2} s^{-1}. Only slight dependencies of the COS flux on soil temperature and water content were detected. The maximum COS uptake occurred around 8 –

9°C and a nearly continuous decline was detected between 10°C and 14.5°C. The measurements done below 9°C showed no dependence on the air temperature.
In contrary, Kesselmeier *et al.* (1999) found a maximum COS uptake at a specific soil water content and at temperatures between 15 - 20°C with a decrease at higher temperatures. This was explained by an enzymatically catalyzed process. Carbonic anhydrase (CA), identified as the controlling enzyme for COS uptake in soil (see 1.4.5.), catalyzes the hydrolysis reaction up to a certain threshold temperature.

In addition, Kesselmeier *et al.* (1999) found COS uptake rates that are up to a factor of 10 higher than the fluxes presented by Steinbacher *et al.* (2004). However, a direct comparison to the data of Kesselmeier *et al.* (1999) is hardly possible due to the different conditions of the measurements, type of soil, and treatment of the soil samples. Unfortunately, in case of parameterization, these results are based on only one soil type. Therefore, there is an urgent need for more data about the exchange capability of COS between soils and the atmosphere.

1.4. Soils

A common criticism of soil taxonomic classifications is that they are mainly based on the subsoil and do not pay attention to the topsoil which is the most important part of the soil for food production, soil management and exchange of gases with the atmosphere.

1.4.1. Dominant soils

The revised legend of the FAO-Unesco Soil Map of the World (FAO, 1988) distinguishes 28 major soil groups, reflecting the main variations in the world's soil cover (Figure 1.4).

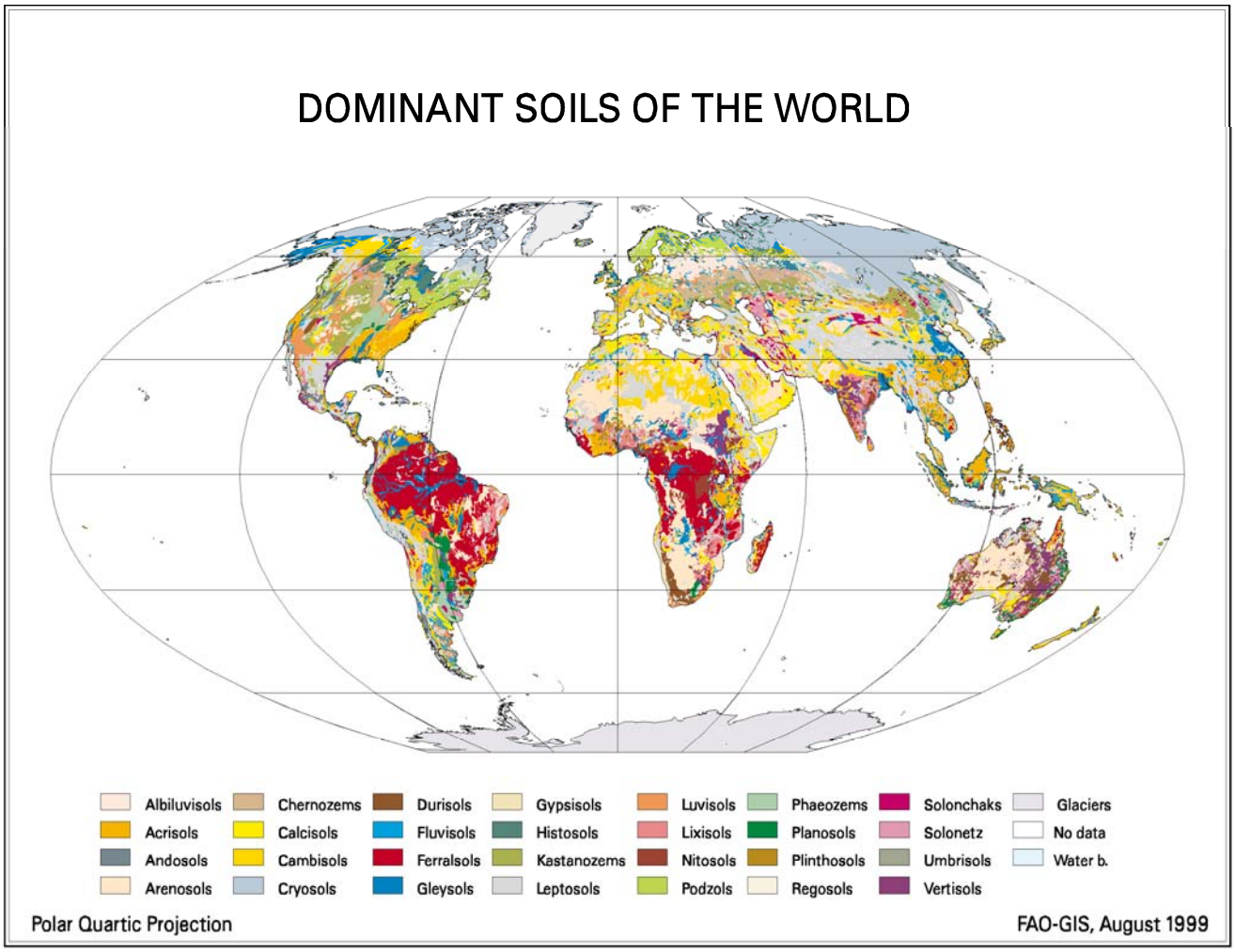

Figure 1.4: FAO-GIS map of the dominant soils of the world (1999), this map distinguishes 28 different dominant soils.

The main soils have been grouped in nine sections which reflect the emphasis on common environmental factors responsible for the soil-forming processes and the properties of the major soil groups.

1. Organic soils: HISTOSOLS
2. Soils conditioned by human influence: ANTHROSOLS
3. Soils conditioned by the parent material: ANDOSOLS, ARENOSOLS and VERTISOLS
4. Soils conditioned by the relief: FLUVISOLS, GLEYSOLS, LEPTOSOLS and REGOSOLS
5. Soils conditioned by their limited age: CAMBISOLS
6. Soils conditioned by seasonally dry or humid subtropical and tropical climate and long evolution: FERRALSOLS, ACRISOLS, LIXISOLS, NITISOLS, PLINTHOSOLS and ALISOLS
7. Soils conditioned by limited leaching (mainly in arid regions): SOLONCHAKS, SOLONETZ, GYPSISOLS, CALCISOLS
8. Soils conditioned by a steppe environment: CHERNOZEMS, KASTONOZEMS, GREYZEMS and PHAEOZEMS
9. Soils conditioned by pronounced movement of clay or ferric and humus materials. LUVISOLS, PODZOLUVISOLS, PODSOLS and PLANOSOLS

On a global scale, the 4 most dominant soils are leptosols (1,655,318,000 ha), cambisols (1,573,402,000 ha), acrisols (996,600,000 ha) and arenosols (901,885,000 ha).

Table 1.3 gives a better general overview of the dominant soils around the world.

Table 1.3: General overview of the most frequent dominant soils used for agriculture around the world (personal communication, Otto Spaargaren, International Soil Reference and Information Center (ISRIC), Wageningen)

Location	***Dominant soil type***
West- and Central-Europe	Cambisols (Lœss landscape)
Mediterranean regions	Gleysols (red soils)
Steppe (Hungary) with a high organic content	Kastanozems (dry) Chernozems (normal)
Wet tropics: - Brazil, Congo - China, South of Changai	Ferrasols, Nitisols (suffered under heavy erosion) Acrisols
Tropics with a dry period (Texas, Kenya, Sudan, Africa, Asia, India)	Vertisols (swelling and shrinking clay soils)
Volcanic soils (Tenerifé)	Andosols (very fertile)

1.4.1.a. CAMBISOLS

Cambisols are moderately developed soils characterized by slight or moderate weathering of the parent material and by absence of appreciable quantities of accumulated clay, organic matter, and aluminum or iron compounds. Cambisols develop on medium and fine textured materials derived from a wide range of rocks, under all climates, any topography and a wide range of vegetation. Although their soil properties may vary widely, they generally have good structural stability, high porosity, good water holding capacity and good internal drainage. Most Cambisols have a moderate to high natural fertility and an active soil fauna. On the whole, Cambisols make good agricultural lands and are intensively used for a wide range of crops (personal communication, Otto Spaargaren, International Soil Reference and Information Center (ISRIC), Wageningen; and (Driessen *et al.*, 2001)).

1.4.1.b. GLEYSOLS

The formation of Gleysols is conditioned by waterlogging at shallow depth for some or all of the year. The prolonged saturation of soils by groundwater in the presence of organic matter results in the reduction of iron that is partly leached out of the soil, and forms a grey, olive or blue-colored subsoil horizon. Subsequent re-oxidation takes place in fissures or cracks in the soil and brown, yellowish or reddish mottles may appear (personal communication, Otto Spaargaren, ISRIC Wageningen).

1.4.1.c. CHERNOZEMS

1. Deep, dark-colored, well drained silty clay loam derived from læss; well developed structure and intensive biological activity (burrowing animals have made krotovinas throughout the profile). They have a calcium carbonate accumulation below 40 cm and high natural fertility.
2. KASTANOZEMS and PHAEOZEMS have an identical structure (wheat, barley, maize; high fertility), but they have a different water content:

   CHERNOZEMS → normal

   KASTANOZEMS → dry

   PHAEOZEMS → wet

   (Personal communication, Otto Spaargaren, ISRIC Wageningen)

1.4.1.d. FERRASOLS

1. Wet tropics and heavy weathered: Very deep, well drained, brownish sandy loam derived from eolian deposits; porous, strongly acid, and has a very low nutrient content and nutrient retention. Different cultivation types are used with mixed cropping systems. These soils contain a high biological activity (termites) and have a weakly expressed soil structure.
2. Tropics with a dry period: Very deep, well drained, dark reddish brown clay developed from limestone; acid, and has a very low nutrient content and nutrient retention. Again different cultivation types are used with mixed cropping systems.

(Personal communication, Otto Spaargaren, ISRIC Wageningen)

1.4.1.e. NITISOLS

Wet tropics and heavy weathered: Very deep, well drained, moderately leached yellowish dark red clay; well structured, with slightly acid to neutral soil reaction. This dominant soil type has high organic matter content (± 15 kg m^{-2}), is a highly fertile soil and is suitable for a variety of land uses.
Commercial farming: coffee, tea, tropical fruits
Also maize, sweat potato, beans
(Personal communication, Otto Spaargaren, ISRIC Wageningen)

1.4.1.f. ACRISOLS

1. Wet tropics: Very deep, well drained, reddish brown to yellowish red clay derived from non-consolidated sedimentary rocks; friable, strongly acid, very low nutrient content and medium nutrient retention, but have high organic matter content. Different cultivation types are used with mixed cropping systems.
2. Tropics with a dry period: Very deep, well drained, red clay with a nearly structureless topsoil and a thin seal on top; strongly acid, and have a low nutrient content and nutrient retention. They have high silt content (> 35%), and reduced permeability due to near absence of macropores (air capacity about 5%). Cultivation: oil palm, rubber, cocoa, coffee, coconut

(Personal communication, Otto Spaargaren, ISRIC Wageningen)

1.4.1.g. VERTISOLS

Tropics with a dry period: Fine textured, having more than 30% of clay, usually smectite, shrink and swell with change in moisture, and have a regular turnover of the soil material, polished shear planes and wide cracks. They have a high nutrient retention and a nutrient content usually imbalanced by dominance of calcium and/or magnesium. Unfortunately, it has poor work ability: too sticky when wet and too hard when dry. Arable farming: main crops are maize, millet and bean, but cotton and sugarcane are the most important ones (under intensive irrigation; Personal communication, Otto Spaargaren, ISRIC Wageningen).

1.4.2. Topsoils

Topsoils are variable in space and time which makes it difficult to classify them. But the topsoil is that part of the soil which is most important for food production, soil management and exchange of gases with the atmosphere.
The factors that influence the characteristics of the topsoils are climate, vegetation and organic matter, topography and physiography, mineral soil constituents, surface processes, and biological and human activity. Based on the dominant features within the topsoils, the topsoil properties are defined.

1.4.2.a. FAO classification

The topsoils are grouped by texture and the following dominant features: organic matter, organic matter status, physical, chemical and biological features, drainage feature, land use, erosion or degradation, external physical conditions, and slope class (Food and Agriculture organization of the united nations, Rome 1998).

In this study the top 5 cm of the soil was used, which indicates that it is important to take a global topsoil map into account instead of the global dominant soil map.

1.4.3. Soil characteristics

1.4.3.a. Soil chemical composition

Soils are ecosystems and some of the main soil processes are biological. Much carbon is locked up in soil organic matter. The decay of this organic matter by soil microorganisms and the release of carbon dioxide and ions is the largest microbial process in soil. Other essential biological processes are the transformations of nitrogen, phosphorus, and sulfur compounds and the mobilization of iron. Plant roots and microbes together virtually control the composition of soil air. Plants profit from a nutrient rich soil, which contains mostly carbon (C), hydrogen (H), nitrogen (N), phosphorus (P), sulfur (S), potassium (K), calcium (Ca) and magnesium (Mg). Each nutrient element has a number of sources in soil. Each nutrient has different cycles, but none of them is closed. Some losses are caused by leaching, erosion, harvesting, and the escape of gases to the atmosphere.

1.4.3.b. Gas diffusion

Gas molecules in soil are in continuous thermal motion according to the kinetic theory of gases, there is also collision between molecules - a random walk. In soil, a concentration gradient causes net movement of molecules from high concentration to low concentration; this drives the movement of gas by diffusion.

Gas diffusion in soil is affected by different soil properties including structure, texture, water and air contents.

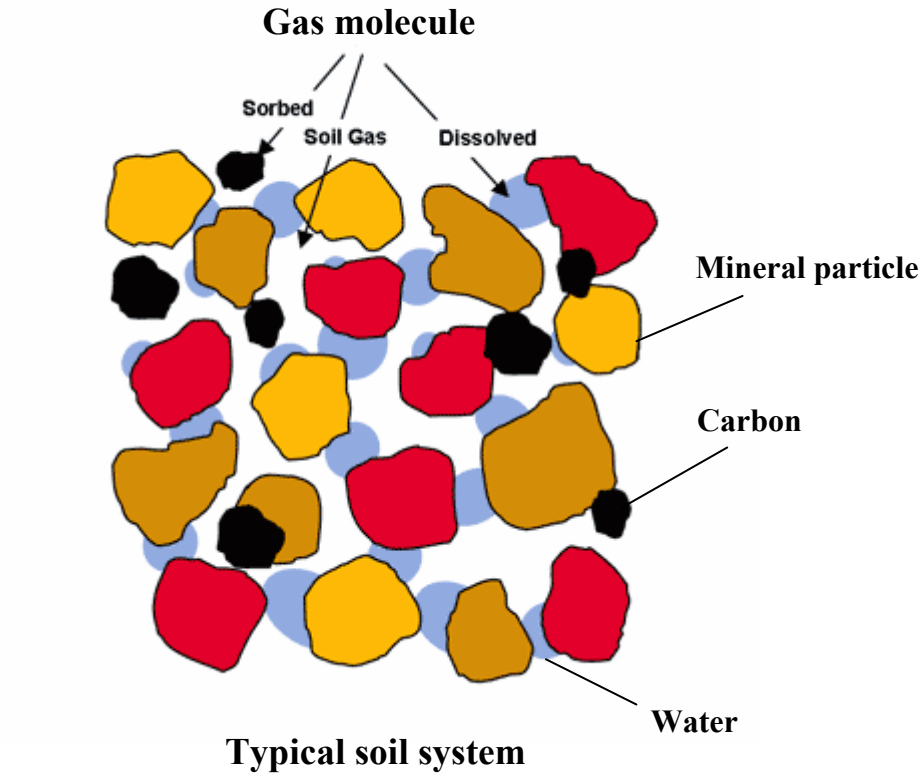

Figure 1.5: A gas molecule partitions itself into four different components (mineral soil particles, carbon, water, and soil gas) (USEPA, 1996, *User's Guide to the VOCs in Soils Presumptive Remedy*).

In natural state, most soil systems comprise four major components: mineral soil particles, natural organic carbon, water, and void spaces filled with soil gas (Figure 1.5). When a gas molecule is released into the soil, some of it volatilizes and becomes part of the soil gas; some of it will dissolve into the interstitial water that resides in and around the soil particles. The amount of gas that volatilizes or dissolves depends on the affinity of the chemical for water. This is defined by its Henry's Law coefficient.

The gas diffusion coefficient (D_P), which depends on air-filled porosity (ε), influences transport, retardations, and degradation of greenhouse gases and other gas molecules in soils (Moldrup *et al.*, 2000b). Moldrup *et al.* (2000a) observed that gas diffusion in sieved, repacked soil appears to be much less soil-type dependent than gas diffusion in undisturbed soil. They also reconfirmed that the Marshall (1959) model better predicts $D_P(\varepsilon)$ in completely dry, repacked porous media than other models do.

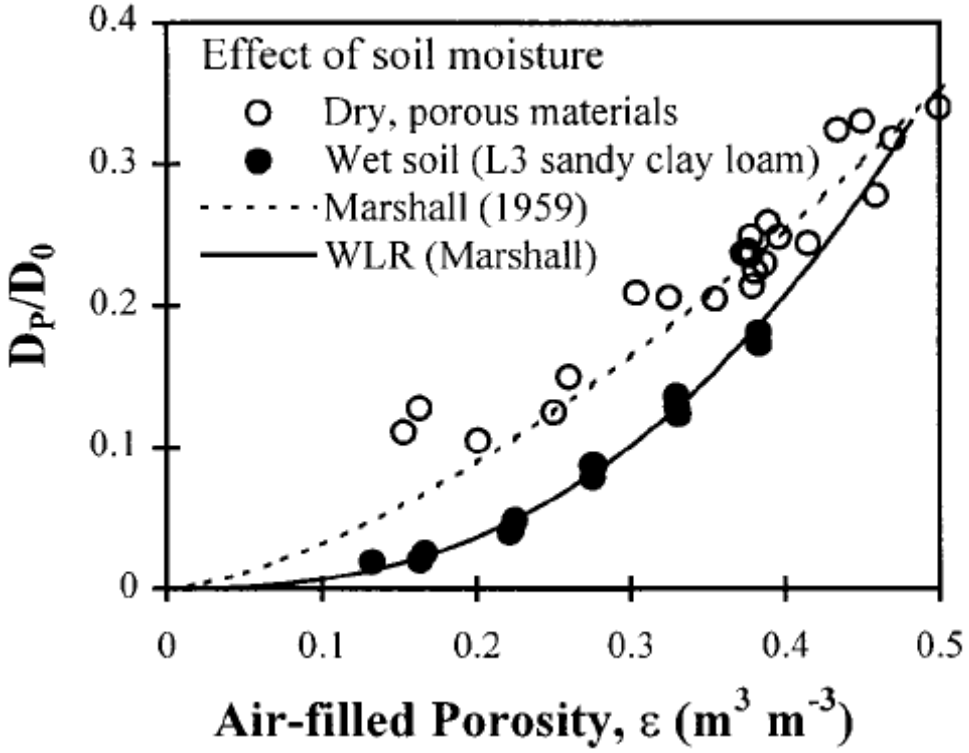

Figure 1.6: Comparison of gas diffusivity in completely dry porous media (open circles) and in wet soil (full circles) with D_P is the gas diffusion coefficient in soil (cm^2 s^{-1}, D_0 is the gas diffusion coefficient in free air (cm^2 s^{-1}), ε is the soil air-filled porosity (cm^3 cm^{-3}). This graph represents predictions by the Marshall (1959) model for dry soil, and the new WLR (Marshall) model for the wet soil (Moldrup et al., 2000b).

Moldrup *et al.* (2000b) also developed a $D_P(\varepsilon)$ model for wet soils by adding a water-reduced linear reduction (WLR) term to the Marshall model (Figure 1.6). Their study implies that the smaller D_P in a wet soil, which is due to water-induced changes in air-filled pore shape and pore connectivity, can be described by a simple, linear function of relative air-filled porosity. The WLR term describes the effects of changing pore shape and configuration in a wet soil compared with a dry soil at the same air-filled porosity.

$$\frac{D_P}{D_0} = \frac{\varepsilon^{2.5}}{\Phi} \quad [1]$$

With D_P, the gas diffusion coefficient in soil ($cm^2\ s^{-1}$); D_0, the gas diffusion coefficient in free air ($cm^2\ s^{-1}$); ε, soil air-filled porosity and Φ, the soil total porosity.

However they emphasize that the WLR (Marshall) model, equation [1], is derived and validated only for sieved, repacked soils, but should not at present be used for high-organic soils, for strongly compacted soils, and for undisturbed soils. For the latter soils, Moldrup *et al*. (2000b) refer to the predictive D_P/D_0 model by Moldrup *et al.* (2000a) that takes into account soil type and macroporosity (Moldrup *et al.*, 2000a).

1.4.3.c. Soil water content (WC)

Water content (WC) is simply the amount of water in a particular piece of soil. Soil water content is commonly expressed as a fraction of the soil dry weight, or sometimes as a fraction of the bulk volume or of the pore space. Conventionally, soil water content is the amount of water that one can drive from a sample of the soil by drying it to steady weight in a 105°C oven. For our study the soil was air-dried at 5°C in order to prevent the death of some of the micro-organisms in the soil.

1.4.3.d. Soil texture

Soil texture is a term commonly used to designate the proportionate distribution of the different sizes of mineral particles in a soil. Few soils consist of mineral particles of a single size class. Usually soils are a mixture of sand, silt, and clay, whose relative proportions determine the soil's texture. According to their size, these mineral particles are grouped into separates, which is a group of mineral particles that fit within definite size limits expressed as diameter in millimeters. The USDA (United States Department of Agriculture) soil textural triangle was designed so that any combination of particle sizes could be included within a textural separate (Figure 1.7). Each corner of the textural triangle represents 100 percent of a size fraction: sand, silt, or clay.

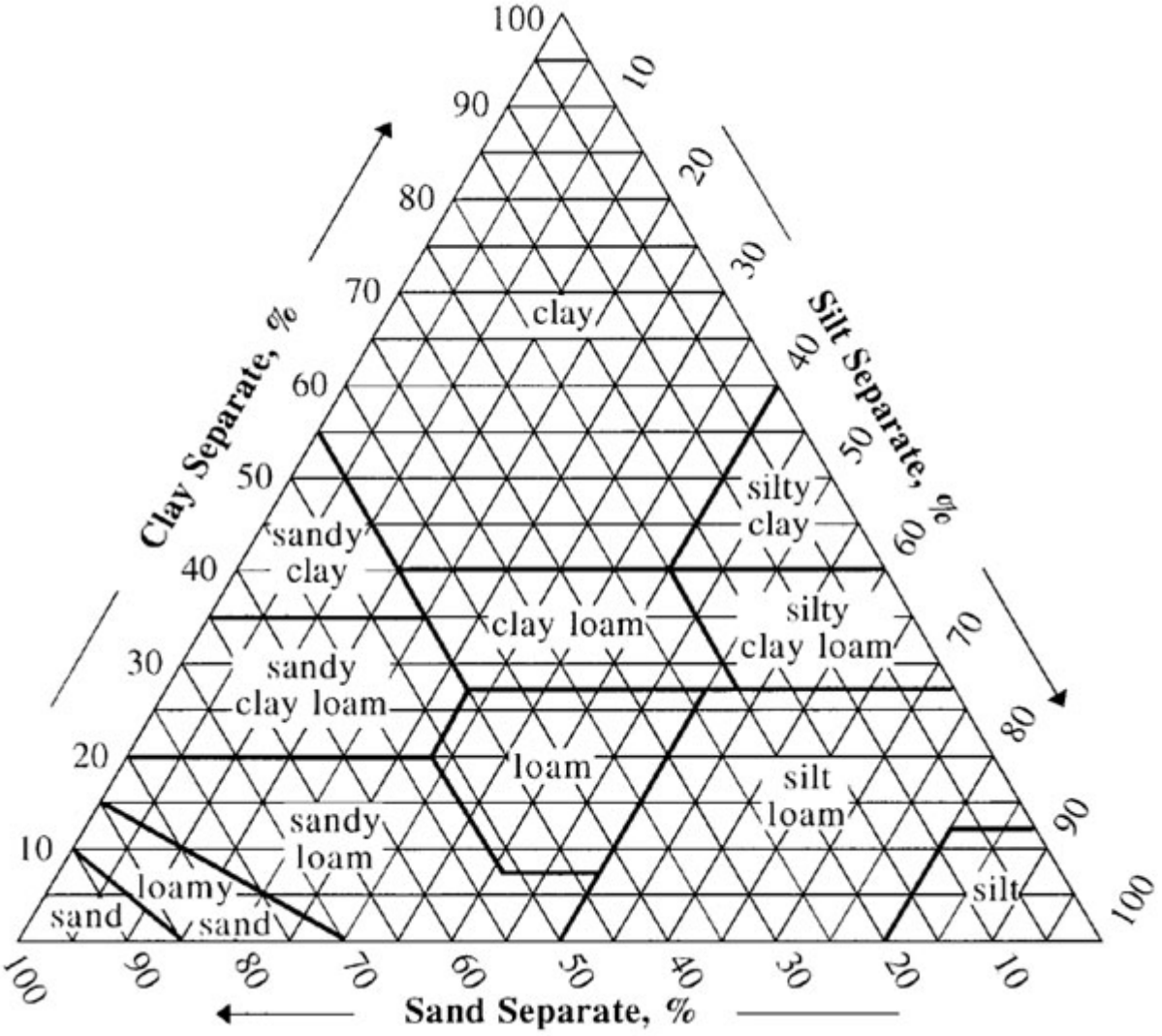

Figure 1.7: This is the USDA soil textural triangle, within the triangle are areas that represent the allowable combinations of the three size separates – sand, silt, and clay – for each textural class name.

1.4.3.e. Water-filled pore space (WFPS)

Pore space exists around individual particles such as sand, silt, and clay or around individual structural units such as soil aggregates. Large sized soil pores are usually filled with air and have therefore a good aeration but poor water holding capacity. Small soil pores are usually filled with water and have therefore large water holding capacity but poor aeration. Soils characterized by small soil pores have more total pore space than soils dominated by large pores. There are two main forms of pore spaces in the soil: aeration pores (> 60 µm diameter) called “macro pores” and capillary pores. The latter are subdivided in available water pores

(0.2 – 60 µm diameter) called "meso pores" and unavailable water pores (< 2 µm diameter) called "micro pores" (Coder, 2000).

In order to calculate WFPS, it is necessary to measure the bulk density. Bulk density is the weight of the soil per unit volume (usually in g m^{-3}).

1.4.4. Soil microorganisms

These soil organisms are the smallest and physiologically and biochemically the most diverse organisms in the soil. They belong to the prokaryotic organisms and more in particular to the Monera or bacteria. Soil microbes are survivors and proliferate rapidly. However these organisms need favorable physical conditions and nutrition to survive. Although conditions rarely favor growth and activity for a long time and mortality is high as cells enter and leave dormancy, enough micro-organisms remain viable to recolonize the soil when conditions improve.

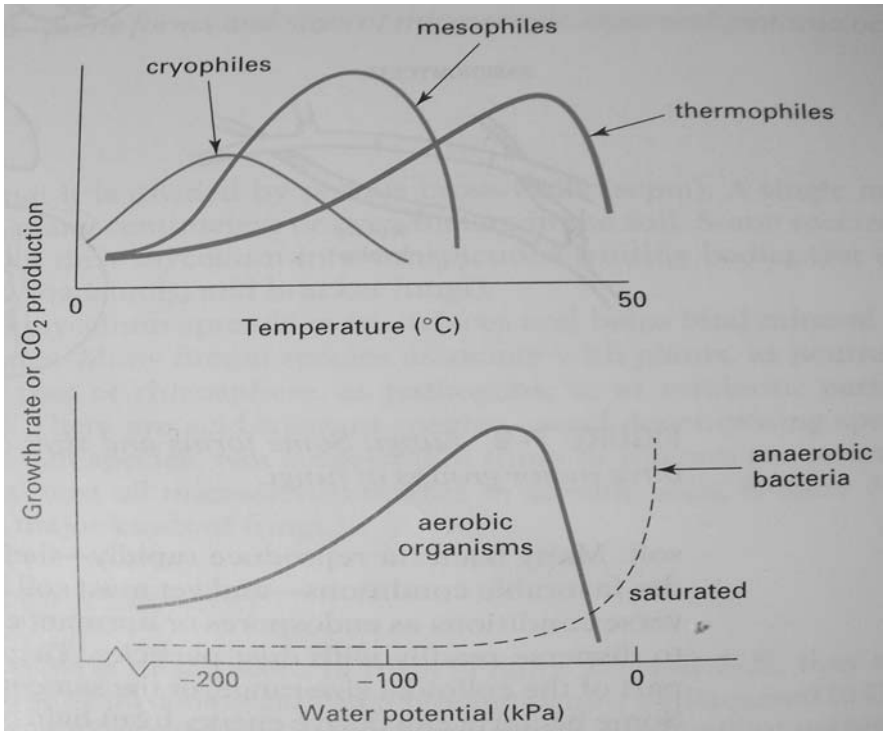

Figure 1.8: Temperature and water requirements of differently adapted bacteria (from Singer M. J. and D. N. Munns (1999) Soils: an introduction).

Soil temperatures fluctuate daily and seasonally, particularly at the soil surface where temperatures commonly range from subfreezing to 45°C. High temperatures, from 35°C upward, can progressively kill cells, depending on the species heat tolerance (Figure 1.8). Cold temperatures, approaching freezing, essentially stop microbial growth, but without killing the organisms. Heat and cold alter the composition of the microbial population in soils. At different temperatures different microorganisms will have their optimal activity. Also soil water conditions are seldom ideal for soil microbes and therefore show a maximal activity at a certain water potential (Figure 1.8).

The nutritional requirements include usable sources of energy and essential elements. Many microorganisms need certain biochemical compounds that they cannot produce for themselves. A fertile topsoil might contain 100 million or more living bacteria per gram of soil. Some bacteria can derive energy from light or from inorganic reactions, some can assimilate nitrogen or sulfur from air (Singer and Munns, 1999).

1.5. The carboxylating enzymes and carbonic anhydrase (CA)

In plants the carboxylating enzymes ribulose-1,5-biphosphate-carboxylase (RUBISCO) and phosphoenol pyruvate-carboxylase (Pep-Co) are able to consume COS by hydrolysis of COS to CO_2 and H_2S (Protoschill-Krebs and Kesselmeier, 1992). Protoschill-Krebs and Kesselmeier (1992) showed that RUBISCO and Pep-Co accelerated COS hydrolysis by the fixation of HCO_3^- and CO_2. This consumption was significantly enhanced by adding CA, which is therefore recognized as the key enzyme for the uptake of COS in higher plants, algae, lichens and soils (Protoschill-Krebs *et al.*, 1995; Protoschill-Krebs *et al.*, 1996; Kesselmeier *et al.*, 1999; Kuhn and Kesselmeier, 2000; Schenk *et al.*, 2004; Yonemura *et al.*, 2005; Notni *et al.*, 2007).

1.5.1. Carbonic anhydrase (CA)

Recent research has demonstrated that CA´s are far more prevalent in prokaryotes and distributed among far more metabolically diverse species than previously recognized (Smith *et al.*, 1999; Li *et al.*, 2004). CA has been found in virtually all mammals, as well as plants and algae, and is fundamental to many eukaryotic biological processes such as photosynthesis, respiration, CO_2 and ion transport, and calcification and acid-base balance (Smith *et al.*, 1999). There are around 14 isoforms of CA identified in mammals to date, in

which CA II is the most widely studied in terms of substrate reaction kinetics and its roles in mammalian physiology. It was even shown that CA´s protected insects in high CO_2 environments but facilitated the toxicity of COS (Haritos and Dojchinov, 2005). CA II is known to metabolize CO_2 to bicarbonate and hydrogen ion at rates among the fastest known for any enzyme with a K_{cat} of 1.4 10^6 s^{-1} at pH 9 and 25°C (Khalifah and Silverman, 1991; Schenk *et al.*, 2004).

CA is a ubiquitous zinc enzyme that accelerates the reversible hydration of CO_2 by a factor of 10^7 as compared to the uncatalyzed reaction. This enzymatic process is very important for all living organisms for the exchange of CO_2 with the atmosphere.
The catalyzed reaction is as follows:

(R4) $CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$

Plant CA´s, which primarily belong to the β-CA family and are evolutionarily and structurally unrelated to the predominantly animal α-CA family, also catalyze the hydrolysis of CO_2 (Hewett-Emmett and Tashian, 1996; Protoschill-Krebs *et al.*, 1996).

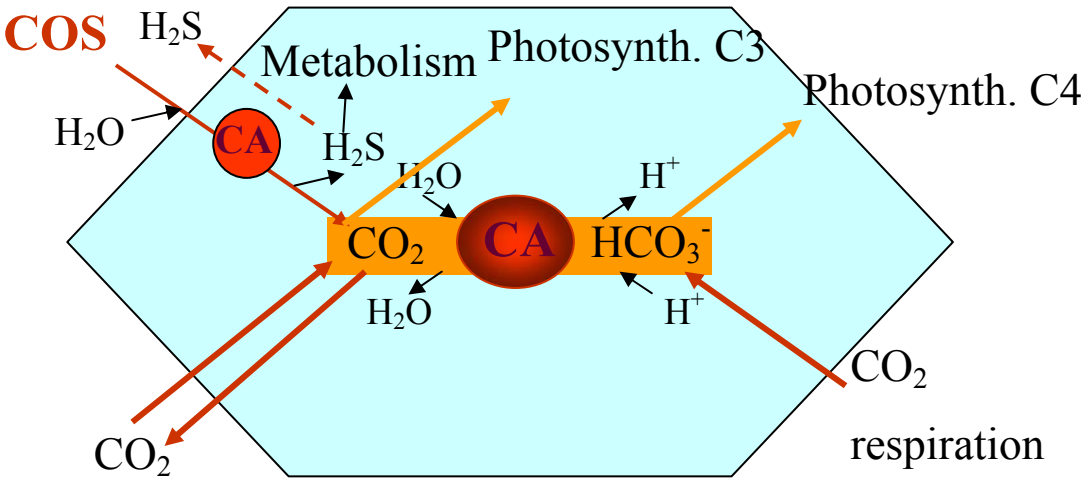

Figure 1.9: Carbonic anhydrase (CA) accelerates the reversible hydration of CO_2, but is also the key enzyme for the uptake and consumption of atmospheric COS and catalyzes the splitting of COS into CO_2 and H_2S (edited from Kuhn (1997)).

Investigations involving the enzyme isolation, inhibition, and induction experiments with different kinds of organisms have provided evidence that CA, besides its role in CO_2 exchange, is the key enzyme for the uptake and consumption of atmospheric COS and catalyzes the splitting of COS into CO_2 and H_2S (Figure 1.9). The activation energy of the nucleophilic attack on COS, which is the rate determining step, is somewhat higher because of the lower electron affinity of sulfur than in comparison to oxygen (Li *et al.*, 2004; Schenk *et al.*, 2004; Haritos and Dojchinov, 2005).

The K_M (Michaelis-Menten constant) value for the consumption of COS by CA was found to be 39 μM. For comparison with the consumption of CO_2 by CA in the same plant species (K_M = 34mM), the affinity towards COS is a thousand times higher than for CO_2. This high affinity for the substrate COS explains how CA is able to overcome the high concentration differences of COS (500 ppt) and CO_2 (350 ppm) in the atmosphere (Protoschill-Krebs *et al.*, 1996). Thus, COS supply rather than the CA content and its activity are the limiting factor for the COS uptake, but the high affinity of CA for COS meets the requirements for the assumption that is responsible for the uptake of COS in higher plants.

CA inhibition experiments also proved that the COS uptake by marine algae was also catalyzed by the enzyme CA. The addition of the CA specific inhibitor ethoxyzolamide (EZ) led to a complete inhibition of the COS uptake by these algae. Despite of this, the COS consumption by marine algae species was estimated to be negligible compared to the photoproduction and hydrolysis of COS in seawater (Protoschill-Krebs *et al.*, 1996; Blezinger *et al.*, 2000).

CA was also found in many soil micro-organisms. The enzyme has been proposed to be involved in CO_2 or HCO_3^- uptake in bacteria that contain a periplasmic CA (Braus-Stromeyer *et al.*, 1997).

A drastic inhibition of COS uptake by soil, after addition of the inhibitor 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ), confirmed the key role of CA in soils. Kesselmeier *et al.* (1999) compared the uptake of COS of the soil sample with and without inhibition of the specific enzyme CA (Figure 1.10).

The addition of the inhibitor EZ to the soil sample resulted in a highly significant ($p < 0.001$) reduction of the COS uptake of more than 50%, showing CA to be one of the dominant factors for the consumption of COS by the investigated soil (Kesselmeier *et al.*, 1999).

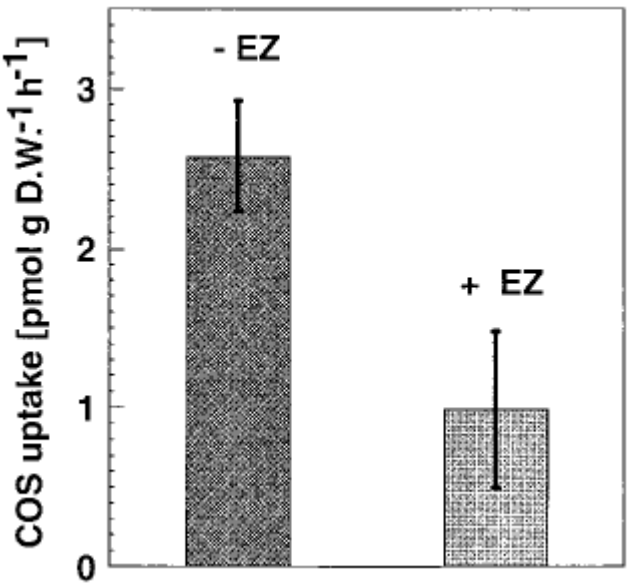

Figure 1.10: Inhibition of COS uptake by the CA specific inhibitor 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ) (Kesselmeier *et al.*, 1999).

1.6. Aim

Since earlier estimates for the uptake of COS by vegetation seem to be underestimated, the global atmospheric budget of COS could become unbalanced (Sandoval-Soto *et al.*, 2005). Therefore it is important to reinvestigate all sinks and sources.

Within this context there is also an urgent need for more data about the exchange capability of COS between soils and the atmosphere. Unfortunately the uncertainty about the uptake of COS by soils is rather large as this knowledge is based on only few results, in case of parameterization only on one soil type (Kesselmeier *et al.*, 1999). Hereby, temperature and soil moisture content were presented as the controlling variables to study the COS uptake by soils.

In the present study our objective was to obtain information about the parameters which are important for the uptake of COS by soils. 5 soils around the world were investigated for their uptake capability of COS in correlation to temperatures between 10°C and 35°C. In addition, for each temperature soil water content (WC) was varied between the maximum water capacity of the soil and 0% WC.

Since enzymatic uptake could be the main cause for the uptake of COS by soils, CA-activity was investigated for all 5 soils using a modified method of Wilbur and Anderson (1948).

2. Materials and Methods

2.1. Soil material: origin

The top 5 cm of the soil is assumed to play the most important role in the gas exchange between soil and the atmosphere. In this PhD-work we decided to concentrate ourselves mainly on arable soils from different sites of the world. We took some soil samples from Mainz (representing the German soil), from the North-East of China, from Finland, from Central Siberia and from Surinam (South-America).

The loose-leaf litter (fallen leaves, twigs …) was cleared away and a soil core was pushed into the soil until it was flush with the surface. The core was dug out making sure the soil remained in the core. The soil was emptied into a Ziploc packet. All this was repeated 10 times in an area less than 10 m radius, placing the soil into the same packet.

In order to determine the bulk density, which is a measure of the soil density and is an important parameter in calculating emissions or uptake, we used the same core. This time it was necessary that the core was inserted vertically and that the core was exactly flush to the soil surface. Thereafter, the core was partially excavated and a lid was placed on the core ensuring that it fitted all the way down. At last, the core was dug out and turned upside down in order to cut the soil in that way that it was flush with the bottom edge of the core.

2.1.1. German soil

These soil samples were obtained from the top 5 cm of an agricultural site near Mainz (Mainz-Hechtsheim; 49° 57′ N, 8° 15′ E), Germany, in March 2004 and June 2006, consisting of sandy clay with low loess content. Transport of the soil samples took only 10 minutes and were immediately stored under 5°C. It is the same arable soil as used for the soil exchange measurements by Kesselmeier *et al.*, 1999. Soil characteristics were determined by the University of Mainz in the laboratory of Micro-analytics.

2.1.2. Chinese soil

These soil samples were obtained from the top 5 cm of an agricultural site from an arid and semi-arid region in the temperate zone of Northeast of China (45° 36′ N, 123° 21′ E) in November 2004. Soil samples were transported during 3 days by train and immediately stored under 5°C. At that time, the land was used as a soybean field. It is a sandy arable soil situated in a region with an annual average temperature of 4.3 °C, with a maximum air temperature of + 37°C in July, and a minimum air temperature of – 32 °C in January.

2.1.3. Finnish soil

These soil samples were obtained from the top 5 cm of an agricultural site near Hyytiälä (61°50′13”N, 24°19′57”E) in Finland. This soil has a moraine origin with a relatively coarse texture and a mean particle size about 0.1 mm. The soil was shipped during 48 hours under cool conditions.

2.1.4. Siberian soil

These soil samples were obtained from the top 5 cm of a forest site in Central Siberia. It is a sandy soil coming from a boreal forest in Zotino along 60° N 89° E. The podzolic soils are mostly characterized by low pH_{H2O} of 4.7 – 5.3. A mono-specific forest of Pinus sylvestris trees dominate the sand region. The climate of the Zotino region is continental with average air temperatures of – 26°C and air temperature minima around – 56°C in January, but daily maxima between May and September may reach 36°C. North Atlantic cyclones are the main source of precipitation. The annual precipitation is also fed by a local water cycle of evaporation and convective storms (Kurbatova *et al.*, 2002; Schulze *et al.*, 2002).

2.1.5. Surinam soil

These soil samples were obtained from a surrounding lowland forest area in Brownsberg (04° 59′ 36” N, 55° 11′ 35” W, Surinam, South America), around 100 km from Paramaribo, the capital of the country. We ensured that the sample site was not disturbed and at least 50 to 100m away from the road. Immediately after sample taking soil samples were transported with an airplane to the Netherlands and transported by car to Germany. During the entire transport samples were kept under 5°C.

2.2. Method of sample taking

Soil samples were obtained from the top 5 cm of three different agricultural sites and two forest sites of the world. The samples were sieved with a stainless steel sieve with a mesh width of 2 mm. The potential water storing capacity (% H_2O g^{-1} dry weight) was determined according to conventional methods (Kuntze *et al.*, 1994; Larcher, 1994). Samples were stored in polyethylene bags under 5°C until the investigations were carried out. Soil WC was controlled by air-drying and by moistening with deionized water (R > 18MΩ cm).

2.2.1. Calculation of Water-filled pore space (WFPS)

WFPS was calculated according to the general particle density (ρ_S), considered to be 2.65 g/cm³ for most of the soils, and the bulk density (ρ_b) (Hillel, 1980; Singer and Munns, 1999). In contrast with the mean general particle density, which is typically constant, the bulk density is highly labile. This is the mass (weigth) of soil per unit bulk volume and is affected by the structure of the soil, that is, its looseness or degree of compaction, as well as by its swelling and shrinkage characteristics. Therefore bulk density was separately determined for each soil type. With this information we were able to calculate the number of pores [2]:

$$f(\#\,pores) = \left[\left(1 - \frac{\rho_b}{\rho_S}\right) \cdot 100\right] \qquad [2]$$

Out of WC and f (# pores) for each soil, the WFPS can be obtained according to equation [3]:

$$\mathrm{WFPS}(\%) = (\mathrm{WC}/\mathrm{f}) \cdot 100 \qquad [3]$$

For each temperature (10°C, 15°C, 20°C and 25°C), controlled by a climate chamber system, a soil sample of 80g was moisturized up to his field capacity and incubated into the cuvette system where it dried out in the course of the constant measurements under near ambient atmospheric COS concentrations. During this period air at the cuvette outlets was sampled and analyzed every 15 minutes.

2.3. Construction and performance of soil enclosures

The intension of these measurements is to analyze the COS exchange between different soils and the atmosphere. These investigations are performed under controlled laboratory conditions with an open dynamic enclosure system. Compressed air is purified and a constant COS concentration is added to the purged air, which is then separately transferred to an empty reference cuvette and a sample cuvette. The exchange of COS is determined by calculating the difference between the COS concentration in reference and sample cuvette at the outlet. Soil samples, moisturized up to their field capacity, were put in the cuvettes where they could slowly dry out from their maximum soil water content (WC) to 0% soil WC. Incubation time was depending on the time the soil needed to dry out from their maximum soil WC to 0% soil WC.

This section will give a detailed description of the system and the **Su**lfur **G**as **A**nalyze**r** (SuGAr).

2.3.1. Purification system

The compressed air was purified in order to guarantee a constant COS concentration in the enclosures and to avoid possible fluctuations (Kesselmeier *et al.*, 1999). The compressed air was purged by passing it through a multistage gas purification system consisting of four 3 L Plexiglas-columns with (Figure 2.1):

(1) Silicagel with humidity indicator to remove the water (1 – 4 mm, VWR International, Darmstadt, article number: 1.01972.1000);
(2) Molecular sieve (0.5 nm, VWR International, Darmstadt, article number: 1.05705.1000) also as a drying agent and to filter trace gases and radicals like ozone;
(3) Charcoal (1 – 3 mm, Carl Roth, article number: 5966.2) to remove COS.

To maintain their quality, the silicagel, the molecular sieve and the charcoal are regenerated by heating them up to respectively 100°C, 300°C and 100°C. The charcoal is also purged with pure Nitrogen 5.0 (Messer, Griesheim).

Figure 2.1: Purification system with four Plexiglas-columns filled with (2 times) silicagel, molecular Sieve and charcoal.

The compressed air (from the MPCh) flew continuously through the purification system with a constant flow of 8 l/min and with a pressure of 1.5 bars. The 3 columns were installed in a separated space build of Plexiglas to assure safety.

2.3.2. Addition of COS

The desired COS mixing ratios were obtained by mixing the purified compressed air with known gas mixtures produced from a permeation device (Haunold, Germany) with COS permeation tubes (VICI Metronics, USA). This was necessary because of the low concentration of COS (500 ppt). The permeation tubes were incubated in a permeation oven under a constant temperature of 50°C. In this way, the permeation tubes were able to produce a constant COS concentration by flushing them with 200 ml/min N_2-flow (N_2 5.0, Westfalen). By using a mass flow controller we were able to regulate the flow, which we need to obtain a constant COS concentration of 500 ppt. Mass flow controllers (MKS, USA) were used to regulate all gas flows.

2.3.3. Enclosure system: cuvettes

Dynamic enclosures and micrometeorological methods are commonly used for measuring reduced volatile sulfur gases by plants and soils. Our measurements were performed with two dynamic enclosures (cuvettes): one enclosing the soil sample (80g) and the other serving as an empty reference. The dynamic enclosure system was chosen in order to measure over a longer time with a constant COS concentration at the inlet of the sample cuvette. These measurements also require some constant factors (constant flow, constant temperatures…) to make a comparison between different soil types possible.

Both cuvettes were coated with a Teflon (FEP) film (Kesselmeier *et al.*, 1999) of which the seams were heat-sealed. FEP Teflon is recognized as the best material for the measurement of sulfur fluxes, especially for COS (Kuster and Goldan, 1987). Two Plexiglas plates, also coated with FEP Teflon, closed the cuvettes. Both cuvettes, with following dimensions: ID, 14.5 cm; length, 9 cm; volume, 1.5 L, were built inside a climate chamber and kept under controlled temperature conditions (between 10°C and 40°C). Figure 2.2 shows the dynamic enclosure system in our laboratory.

Figure 2.2: Reference cuvette (right) and soil sample cuvette (left), all built of Teflon, incubated in a climate chamber.

Each of them was flushed with a total ambient airflow of 2 L min^{-1} containing ± 360 ppm CO_2. To improve mixing of air, the purged air was flushed into the cuvette through a perforated circular Teflon dispenser tube in the middle of the cuvette. The air inside the enclosures was mixed by a propeller covered with PTFE mounted at the upper face of the cuvette and driven by a magnetically coupled motor situated outside the cuvette. All tubing coming from the cuvettes was heated up to 30°C to prevent water vapor condensation. Temperatures were measured with thermocouples (0,005", Chrom-Constantan, Omega, UK). Relative humidity and temperature at the cuvette inlet were determined with a Vaisala sensor (model 133Y, Vaisala, Helsinki, Finland).

The temperatures shown in each experiment represent the incubation temperatures or air temperatures in the sample cuvette. Soil temperatures, measured for some of the experiments, showed only slight deviations under extreme conditions, such as high air temperatures or high soil WC. Soil temperatures were not shown since the COS exchange at higher soil WCs was much smaller for all experiments. Incubation temperatures and soil temperatures were therefore considered as the same.

2.3.4. Sampling and analysis

As already mentioned above, the exchange data of COS were obtained in high time resolution with a fully automated analytical **S**ulphur **G**as **A**nalyze**R** (SUGAR; more detailed information in (von Hobe *et al.*, 2001)) performing an analysis every 15 minutes. The system is build by the Max Planck Institute for Chemistry in Mainz (von Hobe, 2000). COS was fully automatically sampled by cryogenic trapping and analyzed on a gas chromatograph equipped with a flame photometric detector according to Hofmann *et al.* (1992).
The cryotrap is constructed with a stainless steel Silcosteel tube (Silcosteel; Restek; Length; 20 cm; ID, 2 mm), which is also silanized at the inside, and filled with Chromosorb 45/60 W (Fa. Supelco) used as absorbent (Figure 2.3). The cryotrap is cooled down with a Cryotiger (Cooling system, Helix Polycold Systems Inc., USA) to a temperature between –130°C and –150°C (Hoffman *et al.*, 1992).

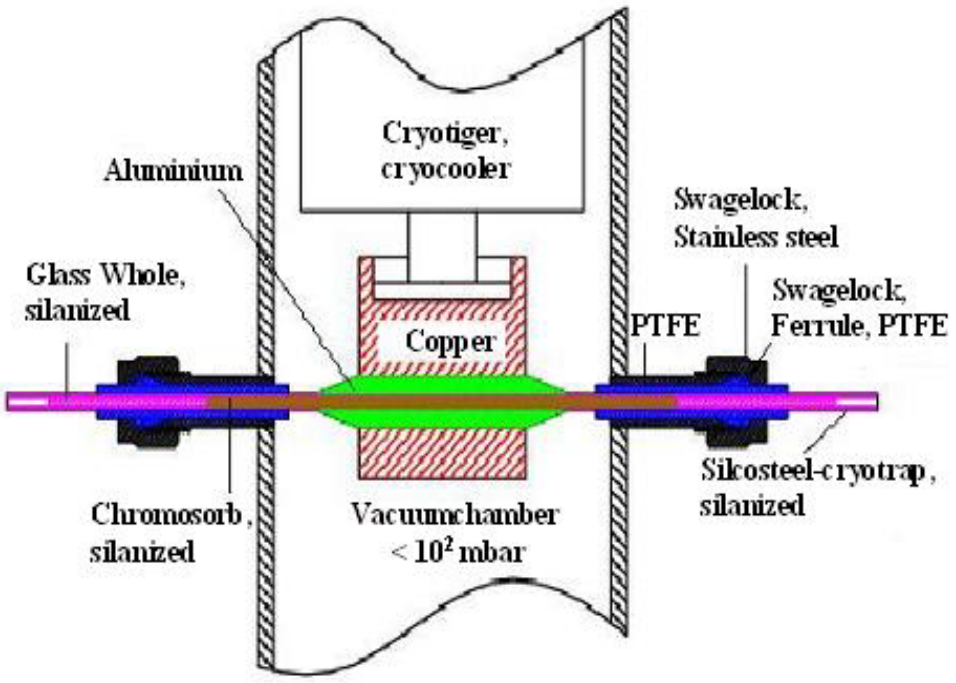

Figure 2.3: Schematic representation of silcosteel-cryotrap (edited (Sandoval-Soto, 2002)

Air is separately sampled from the outlet of each cuvette and trapped by varying heating on the cryotrap, followed by injection into the gas chromatographic system where it is analyzed. For each analysis 100ml/min of cuvette air is sampled over 10 minutes. Sampling was achieved by a Membrane pump (N811 KNDC 24V, KNF Neuberger GmbH, Freiburg). More details concerning this sampling and analyzing technique are described by von Hobe *et al.* (2001). A carrier gas (He 5.0) flow of 20 ml/min was used. The separation of COS took place on a 1.8 m long FEP Teflon column (ID, 1/8") which was packed with 60/80 Mesh Carbopack B / 1.5 % XE 60 / 1.0 % H_3PO_4 (Fa. Supelco). The analysis lasts for 5 minutes with a temperature program as follows:

- 1 minute isotherm at 50°C
- 4 minutes isotherm at 124°C
- 10 seconds at 50°C

The detection of sulfur compounds was made with at flame photometric detector (FPD) and the signal was multiplied by a photomultiplier (Farwell and Barinaga, 1986). The detection was based on the formation of excited S_2-molecules, which fell back into the ground state when a chemiluminescence radiation of 394 nm was emitted. Excited S_2-molecules were formed when sulfur compounds were incinerated in a hydrogen-rich oxygen or air flame.

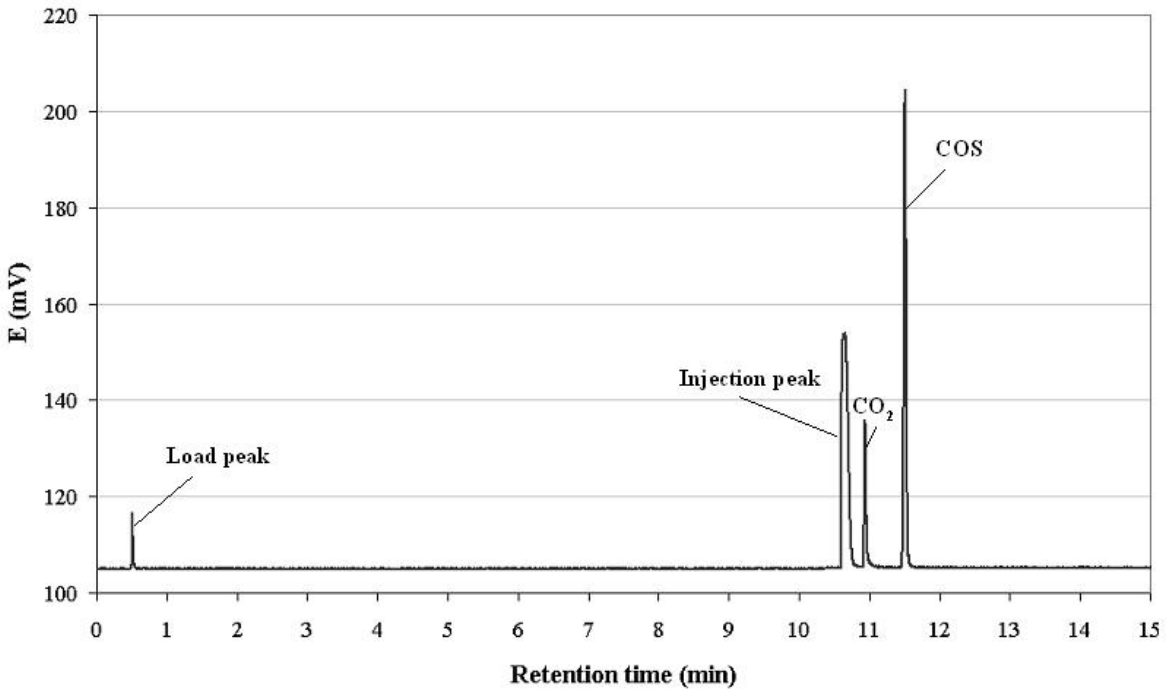

Figure 2.4: A normal chromatogram with the COS-peak.

Data were processed and stored in ASCII-format with a GC analysis software program (ELAB, OMS Tech, USA; Figure 2.4).

2.3.5. Calibration and reproducibility

2.3.5.a. Calibration

The COS signal was calibrated for each analysis by creating a set of 5 different COS concentrations using a permeation tube (VICI Metronics, USA). This permeation tube was kept constantly at 25°C in a permeation oven; build at the MPI for Chemistry, Mainz. Calibration was simultaneously performed for methylmercaptane (CH_3SH), dimethylsulfide (DMS) and carbon disulfide (CS_2) (Figure 2.5). A constant flow of 200 ml/min of air (purified and dried with a nafion dryer) flew constantly through the devices.

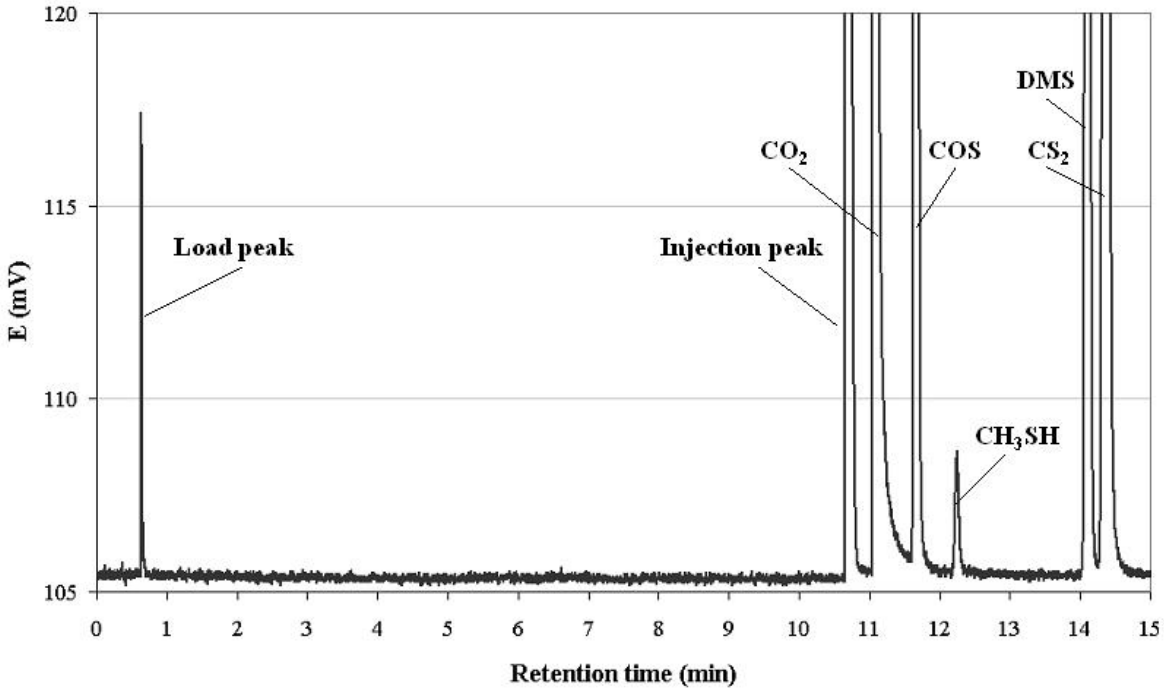

Figure 2.5: Calibration chromatogram at 2.5 ml/min (approximately 500 ppt for COS): shows the retention time of each sulfur gas.

The concentration of the COS-calibration gas (and the other sulfur gases) is determined by means of the permeation rate and the airflow. The permeation rate is calculated by weighing the permeation tube in regular intervals (every month) to determine the weight loss (Figure 2.6).

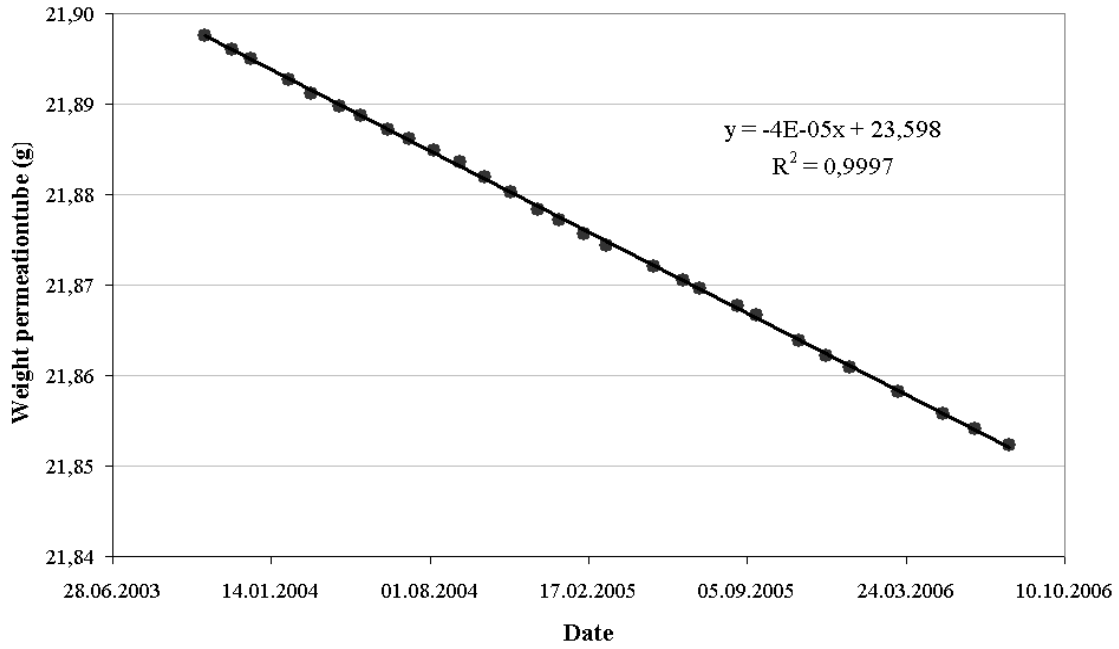

Figure 2.6: Weight loss of the COS permeation tube from 20-10-2003 until 31-07-2006.

The calibration curve is compiled out of the logarithmic calibration concentrations of COS and the concurrent, also on a logarithmic scale, peak areas. The calibration curve is then determined by means of linear regression. In this way the peak area from the chromatograms of reference and sample cuvette air are calculated (von Hobe, 2000). The following figure shows an example of a calibration curve for SUGAR.

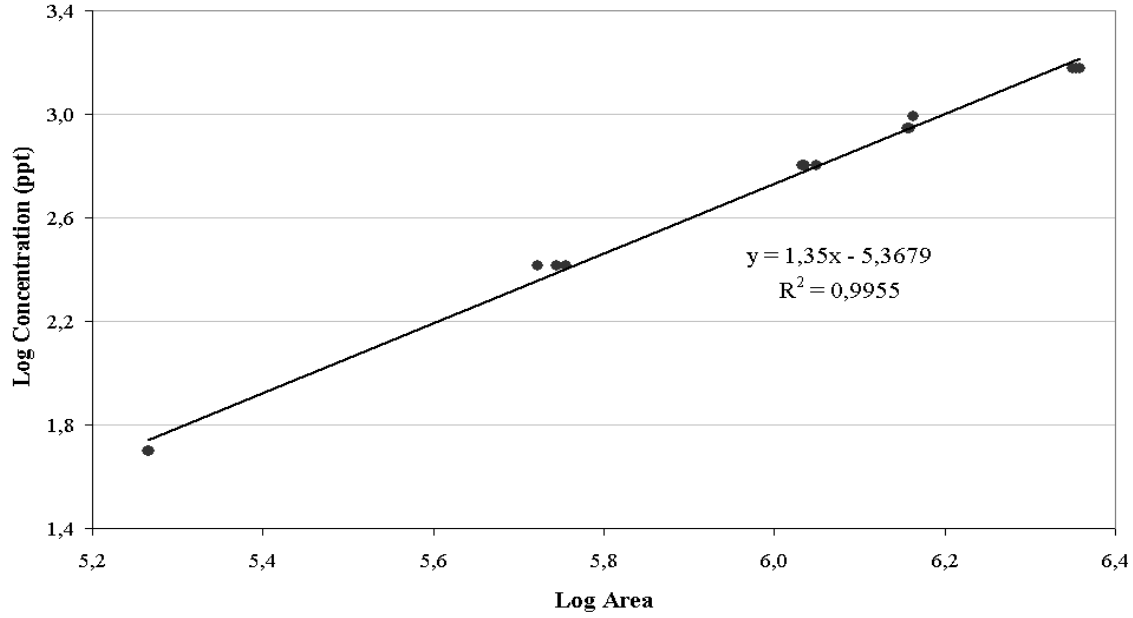

Figure 2.7: COS-calibration curve for 5 different COS-concentrations using a permeation device

2.3.5.b. Reproducibility

Despite all problems (Chapter 2.3.7), SUGAR has a good reproducibility for all 4 sulfur compounds (COS, CH_3SH, DMS and CS_2).

To demonstrate the reproducibility of SUGAR, a zero gradient test was performed by sampling one common standard gas mixture comprising 4 different reduced sulfur compounds. A total number of 20 samples were taken, switching consecutively between reference and sample cuvette (Figure 2.8).

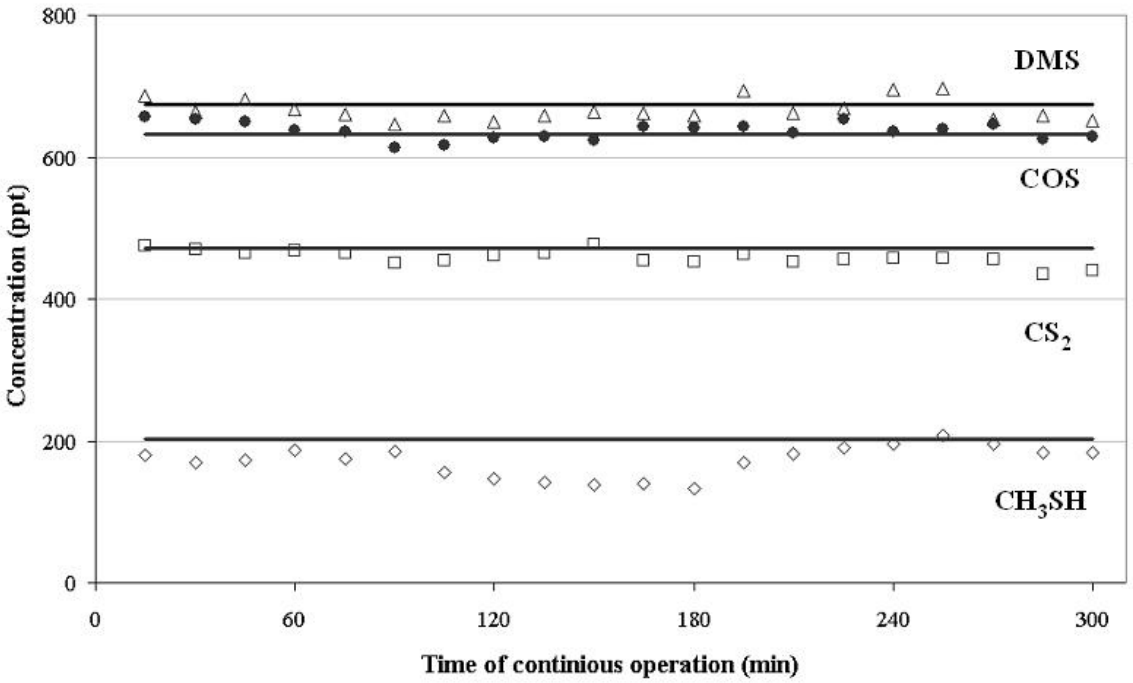

Figure 2.8: Repeated SUGAR measurements (COS: 637 ± 12 ppt, σ_{rel} = 1.9 %; DMS: 667 ± 15 ppt, σ_{rel} = 2.2 %; CH_3SH: 172 ± 21 ppt, σ_{rel} = 12.4 %; CS_2: 458 ± 10 ppt, σ_{rel} = 2.2 %, represented by symbols) on a given standard from a permeation oven (COS: 632 ppt; DMS: 675 ppt; CH_3SH: 202 ppt; CS_2: 471 ppt, represented by lines) to test accuracy and reproducibility.

2.3.6. Error estimation of carbonyl sulfide

The relative precision of the measurements was 1.9%, based on the reproducibility presented in figure 2.8 (σ_{rel}).

The overall absolute accuracy is estimated according to the law of error propagation [4] (Doerffel, 1984) and is estimated to be 5.4%.

$$\sigma_F = \sqrt{\frac{\left[\left(c_{in}\sigma_{in}\right)^2 + \left(c_{out}\sigma_{out}\right)^2\right]}{\left(c_{out} - c_{in}\right)^2} + \sigma_Q^2 + \sigma_A^2} \qquad [4]$$

The following assumptions were made to calculate the errors of the COS exchange rates:

- 1.9% error for the measurements of the COS concentrations c at the cuvette inlet σ_{in} and cuvette outlet σ_{out},
- 5% error in the cuvette flow measurements σ_Q based on the theoretical error of the mass flow controllers, and
- 0.5% in the dry weight estimation σ_A. On the basis of these values we estimated the total error σ_F of the COS exchange rates.

2.3.7. Instrumental details

SUGAR is still a prototype instrument and not yet commercially developed. Therefore, a good knowledge of all details is required to obtain high sensitivity measurements. Some important details which have to be considered are mentioned in this section.

1. Maintenance of the different flows is important for the accuracy and reproducibility of the measurements. For example, in order to achieve a constant flow of 100 ml/min over 10 minutes, sample/reference air is preferred to be almost water free. Otherwise, water can freeze on the trap and block the constant sample/reference flow. A short period of heating can solve this problem, if this is not effective enough, it is necessary to change the cryotrap´ internal material (chromosorb). Moreover, constant carriergas flow and flows of synthetic air and hydrogen have to be assured. On the other hand, the sensitivity of the measurements is also highly depended on the way the cryotrap was installed (Figure 2.3).

2. A vacuum of at least 10^{-3} mbar has to be achieved, to assure a Cryotiger (cooling system) temperature of at least -130°C, which is necessary for trapping COS on the cryotrap.
3. GC-columns mostly have a lifetime of 1 year and have to be exchanged.

Nevertheless, the SUGAR-instrument can perform high sensitivity measurements and has a good detection limit if all the parts are functioning and no problems occur.

2.4. Exchange calculations

2.4.1. COS uptake (F) and deposition velocities (V_d)

Exchange rates were calculated based on the difference between reference and sample cuvette. The gas exchange rate (F) [pmol * g^{-1} * h^{-1}] was calculated according to equation [5] from the measured concentration difference ($\Delta c = c_{sample} - c_{ref}$), the chamber flush rate (Q) and the soil dry weight (dw).

$$F = \Delta c \cdot \frac{Q}{dw} \qquad [5]$$

The gas exchange rate (F) could also be calculated as follows in equation [6] with ($\Delta c = c_{sample} - c_{ref}$) as the measured concentration difference, (Q) as the chamber flush rate and (A) as the soil surface.

$$F = \Delta c \cdot \frac{Q}{A} \qquad [6]$$

Possible fluctuations of COS mixing ratio's were eliminated by normalizing our data to atmospheric concentrations by calculating deposition velocities (V_d in mm s^{-1}) in relation to soil WC, water-filled pore space (WFPS) and temperature.

All measurements were performed with 80g of soil, with exception of the German arable soil, of which the measurements were carried out with 200g of soil in the same cuvette. Kesselmeier *et al.* (1999) found a linear correlation of COS exchange and soil mass up to 200g soil per cuvette, which shifted to a saturation-like exchange behavior with increasing soil masses between 200 and 400g. This implies that deposition velocity data of the German

soil could be recalculated to 80g of soil in order to compare the data of all soils. Therefore, deposition velocities calculated in this study account for 80g of soil with a soil surface of 165.13 cm².

2.4.2. Algorithmic description of the COS uptake

An algorithm had to be developed to fit our laboratory data in order to give the best description for the COS exchange dependence on soil WC and WFPS as well as temperature. The COS uptake (F) and the deposition velocity (V_d) at 80g of soil was best described by the algorithm [7] developed by Meixner and Yang (2006). They used this algorithm to describe NO emissions from soils and higher plants.

$$V_d(WC) = a \cdot WC^b \cdot \exp(-c \cdot WC) \quad [7]$$

The algorithm [6] is described for the dependence of V_d on soil WC, but also accounts for WFPS and temperature dependence.

The parameters a, b and c are related to observed values by

$$a = \frac{V_d(WC_{opt})}{\left[WC_{opt}^{\ b} \cdot \exp(-b)\right]} \quad [8]$$

$$b = \frac{\ln\left[V_d(WC_{opt}) / V_d(WC_{upp})\right]}{\left[\ln(WC_{opt}/WC_{upp}) + (WC_{upp}/WC_{opt} + 1)\right]} \quad [9]$$

$$c = \frac{-b}{WC_{opt}} \quad [10]$$

Where WC_{opt} is the soil WC at which the maximum V_d is observed; $V_d(WC_{opt})$ equals $\max[V_d(WC)]$; and WC_{upp} is the soil WC at which $V_d(WC) = V_d(WC_{upp}) \approx 0$ for $WC > WC_{opt}$.

Numerical values for the parameters a, b and c can be determined by minimizing the sum product of the difference between measured and fitted data points.

2.5. Determination of the enzymatic activity of Carbonic anhydrase (CA)

The determination of the activity of the enzyme Carbonic anhydrase was carried out according to the method of Wilbur and Anderson (1948). This method was based on the pH-drop caused by the reaction between H_2O and CO_2, catalyzed by CA. The time was measured in which the pH drops from pH 8.20 to pH 7.70, both for the catalyzed (T_e) and non-catalyzed reaction (T_0) (Wilbur and Anderson, 1948). The enzyme CA was present in a Bicine Buffer of pH 8.2 and adding a CO_2-saturated solution started the reaction, this represented the catalyzed reaction. In contrast, the non-catalyzed reaction occurred without CA. The time difference between the two reactions was used to calculate the enzymatic activity of CA (in units):

$$\text{Activity}_{CA} = \left(\frac{T_0}{T_e}\right) - 1 \qquad [11]$$

With:

T_0 : the time in which the pH drops with 0.5 in the non-catalyzed reaction

T_e : the time in which the pH drops with 0.5 in the catalyzed reaction

This method was, in our knowledge, never carried out for soil samples; therefore we adjusted some steps in the method to get the best reproducibility we can reach. Further adjustment is still needed.

The method and the chemicals used are described in the following section.

2.5.1. The Bicine Buffer

The Bicine Buffer was composed in Milli-Q-Water (R 18 MΩ) with the following concentrations of chemicals:

- 50 mM Bicine $C_6H_{13}NO_4$
- 10 mM NaCl
- 1 mM EDTA (Ethylene-diamine-tetraacetic acid)

- 0.1 mM PMSF (8-Phenylmethylsulphonylfluoride)

Because PMSF was badly soluble in water, PMSF was solved in Isopropanol. From this stock-solution, the corresponding volumes were added to the buffer solution.

- 1 M NaOH

This solution is used to adjust the buffer to pH 8.2.

- 5 % PVP (Poly-1-vinyl-2-pyrrolidon)

PVP was added before the pH of the buffer was adjusted to 8.2.

2.5.2. CO_2-saturated solution

The CO_2 solution was adjusted with the equipment showed in figure 2.9. During at least 40 minutes 100 % CO_2 gas (99.995 Vol %, Westfalen AG Worms) was bubbled through the Milli-Q Water (R 18 MΩ) until saturation was reached. This resulted in a CO_2 concentration of 76 mM at 0°C and a standard pressure of 1 atm (Gmelin, 1977). Samples were taken with an Eppendorf 1 ml pipette. The pipette tip was also cooled at 0°C prior to sample taking.

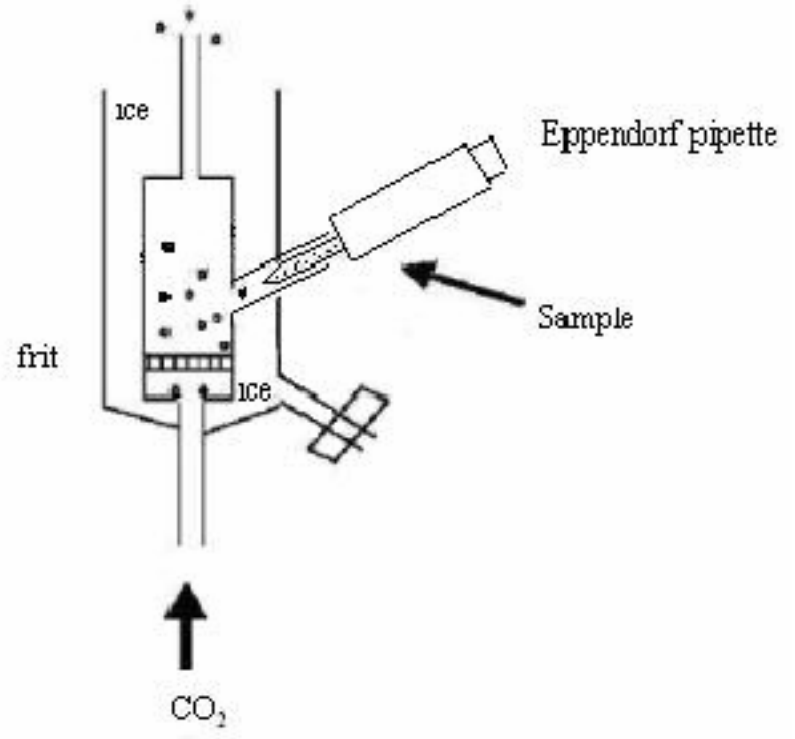

Figure 2.9: Equipment used to produce a CO_2-saturated solution. The CO_2-solution is cooled on ice (0°C).

2.5.3. Preparation of the soil sample

The soil, to be analyzed, was first sieved with a stainless steel sieve with a Mesh wide of 2 mm, pounded in a mortar and stored at 2°C. A sample of 400 mg pounded soil was incubated on ice for 10 minutes in 4 ml of Bicine buffer.

2.5.4. Electrometric determination of CA-activity

The determination of CA-activity takes place at 0°C. The glass jar, with a volume of ca. 15 ml, has a sealed opening for the pH-electrode and a separated tube where the 2 ml CO_2-saturated solution is injected. A magnetic stirrer is used to homogenize the solutions.
For the non-catalyzed reaction (T_0), 8 ml of Bicine buffer is incubated in the glass jar for 10 minutes. For the catalyzed reaction (T_e), 4 ml of Bicine buffer is added to 4 ml of soil sample and incubated in the glass jar for 10 minutes. Adding 2 ml of the CO_2-saturated solution starts the reaction.
The pH is measured with a pH-Meter (pH-Meter 537 Fa. WWT, Weilheim) and a pH-electrode (INGOLD U-455-ST Fa. Ingold). This pH-Meter is connected to a software program (ELAB, OMS Tech, USA) that can transmit the data. Before each group of measurements is carried out, the pH-Electrode has to be calibrated with the calibration buffers pH 4 and pH 7 (mainly daily). Figure 2.10 represents a scheme of the equipment used for the determination of carbonic anhydrase.

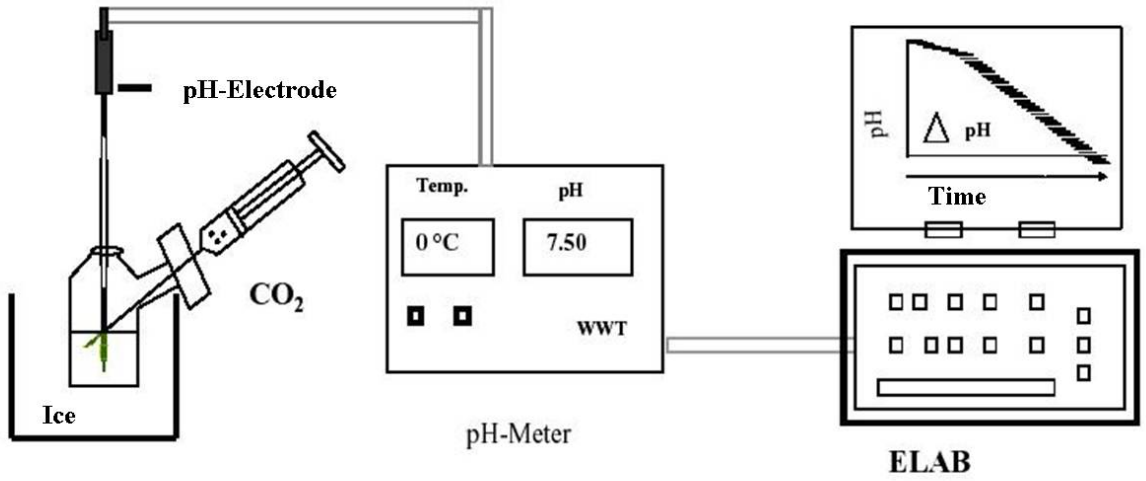

Figure 2.10: Equipment used for the determination of carbonic anhydrase in soil samples.

2.6. pH screening

The pH of all investigated soils was determined according to the method described by (Anderson and Ingram, 1993):

- 50 ml of deionized water (R > 18MΩ cm) was added to 20 ± 0.1 g soil;
- The mixture was stirred for 10 minutes, followed by 30 minutes of rest and stirred again for 2 more minutes;
- After calibrating the pH-Meter (pH-Meter 537 Fa. WWT, Weilheim), same procedure as described in 2.5.4, the pH of the supernatant liquid was measured.

3. Results

In this study five different soils around the world were investigated for their exchange of carbonyl sulfide (COS) between soils and the atmosphere. Deposition velocities (V_d) instead of uptake rates were used in order to eliminate the influence of the fluctuations of COS mixing ratios by normalizing our data to atmospheric concentrations. Furthermore, deposition velocities of COS for 80g of all soils were compared in relation to their soil water content (WC), temperature and water-filled pore space (WFPS). These factors seem to be the three most important parameters to characterize the uptake of COS by soils and are therefore considered in this study. Moreover, enzymatic activity of carbonic anhydrase (CA) in all soils was qualitatively identified with a modified method of Wilbur and Anderson (1948).

3.1. German soil

The study from Kesselmeier *et al.* (1999) already investigated the uptake of COS by a German soil from an agricultural field in Mainz-Hechtsheim, which allowed them to parameterize the uptake in relation to the ambient COS concentration, soil WC and air temperature. In order to demonstrate the constant characteristics of a soil, we reinvestigated the same German arable soil (same site; 49° 57′ N, 8° 15′ E). However, our measurements were performed in high time resolution and therefore allowed a more exact statistical approach. Chemical and physical soil characteristics (Table 3.1) were determined by the University of Mainz in the laboratory of Micro-analytics.

Table 3.1: Chemical and physical characteristics, determined at the University of Mainz in the laboratory of Micro-analytics.

Properties	German soil
C_{total}, wt%	2.22
S_{total}, wt%	0.022
N_{total}, wt%	0.156
Field capacity, % H_2Og^{-1} DW	52.0
Bulk density, g cm^{-3}	1.60
Calculated maximum WFPS, %	124.94
pH at 25°C	7.58

3.1.1. COS exchange in relation to soil WC at different temperatures

Figure 3.1 shows the COS uptake rates in relation to the soil WC as found for the German soil. Each data point represents the mean value of at least 5 measurements with their standard errors ($\sigma/\sqrt{n}$). Soil WCs between 9 and 14% resulted in a maximum of COS uptake, but further increases in the soil WC led to a decrease in exchange. A steep decrease occurred at low soil WCs.

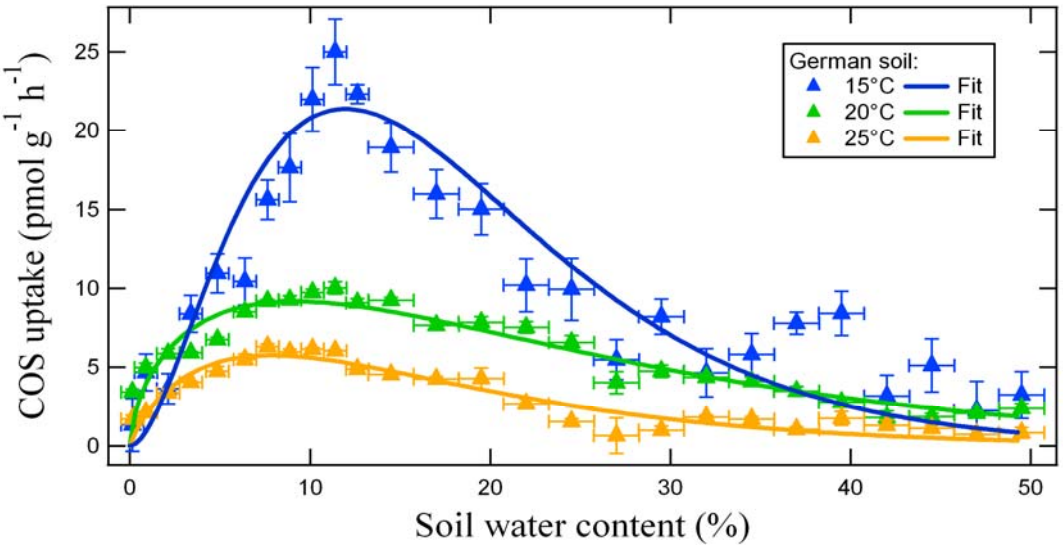

Figure 3.1: COS uptake rates (pmol g^{-1} h^{-1}) for the German arable soil in relation to the soil WC (%) at 15°C, 20°C and 25°C. The optimum of the COS uptake ranges at around 11.5%. Each data point represents the mean value of at least 5 measurements with their standard errors.

The experiment was carried out at an ambient concentration of approximately 1100 ppt to ensure reliable data at low uptake rates (at dry and wet conditions). Although, since Kesselmeier *et al.* (1999) demonstrated that a positive linear correlation exists between the COS uptake and the ambient concentration up to these ranges, we compared all the soil data by calculating the deposition velocity (V_d). This eliminated the influence of atmospheric COS mixing ratio fluctuations.

These measurements were carried out with 200g of German arable soil. In this manner it was possible to compare our findings directly with those of Kesselmeier *et al.* (1999). All further measurements were performed with only 80g of soil per cuvette. Kesselmeier *et al.* (1999) found a linear correlation of COS exchange and soil mass up to 200g soil per cuvette, which shifted to a saturation-like exchange behavior with increasing soil masses between 200 and

400g. Therefore, the data for the German soil was recalculated to 80g of soil (Figure 3.2), which allowed us to compare this data with all further measurements. Maximum V_ds in the range of 0.7 – 0.9 mm s^{-1} for 80g of soil were found at the optimum temperature of 15°C and a soil WC of 11.5%.

The German arable soil had the highest field capacity of all soils. Since the soil dried out from the maximum soil WC to 0% during the incubation time, duration of the measurements was determined by maximum soil WC and temperature. In order to give an idea about the incubation time of each soil sample, measurement times in minutes are given for each soil and at each temperature. The incubation times for the German arable soils were 8143 min, 5987 min and 4385 min at 15°C, 20°C and 25°C, respectively.

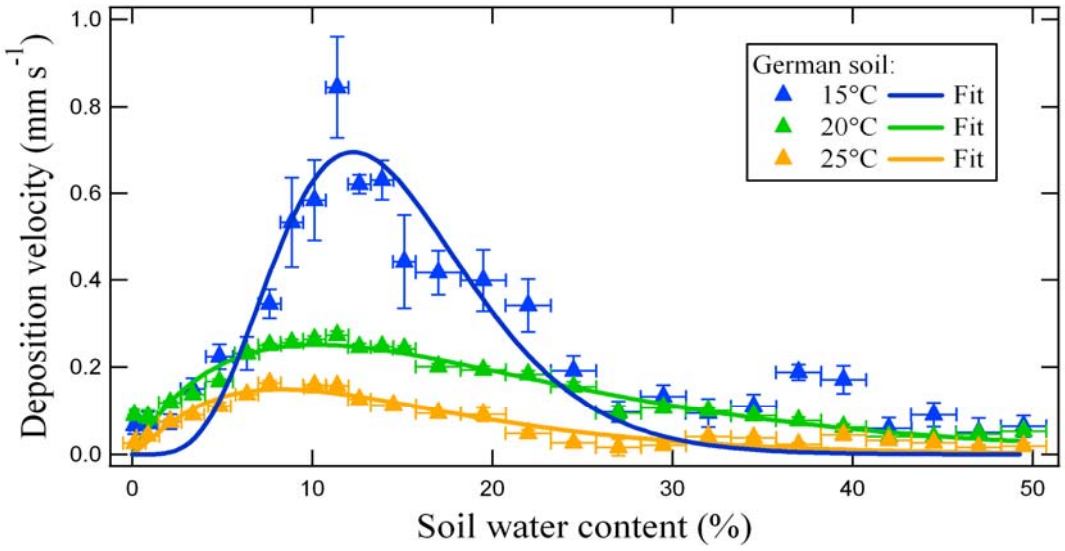

Figure 3.2: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to soil WC (%) for the German arable soil at 15°C, 20°C and 25°C for 80g of soil per cuvette. Each data point represents the mean value of at least 5 measurements with their standard errors.

The mathematical equation [7] developed by Meixner and Yang (2006) gave the best fit to describe the COS exchange dependence on soil WC and WFPS (see section 2.4.2). Thus the V_d for 80g of soil per cuvette at a given temperature was described as a function of WC_{opt}, this is the soil WC at which the maximum V_d is observed and as a function of WC_{upp}, this is the soil WC at which $V_d(WC) = V_d(WC_{upp}) \approx 0$ for $WC > WC_{opt}$. The mathematical fit described well the measured data points, but took the maximum V_d less into account, although this data point represented the mean value of at least five measurements and should be considered in the discussion.

3.1.2. The importance of water-filled pore space

In order to include the soil texture as an important parameter for the COS uptake, we investigated the relation between V_d and the water-filled pore space (WFPS), a parameter depending on soil structure and WC (Figure 3.3). WFPS was calculated according to the general particle density (ρ_S), considered to be 2.65 g/cm³ for most of the soils, and the bulk density (ρ_b) (Hillel, 1980), which was separately determined for each soil (see 2.2.1). V_d optima at each temperature shifted to a WFPS at around 29%.

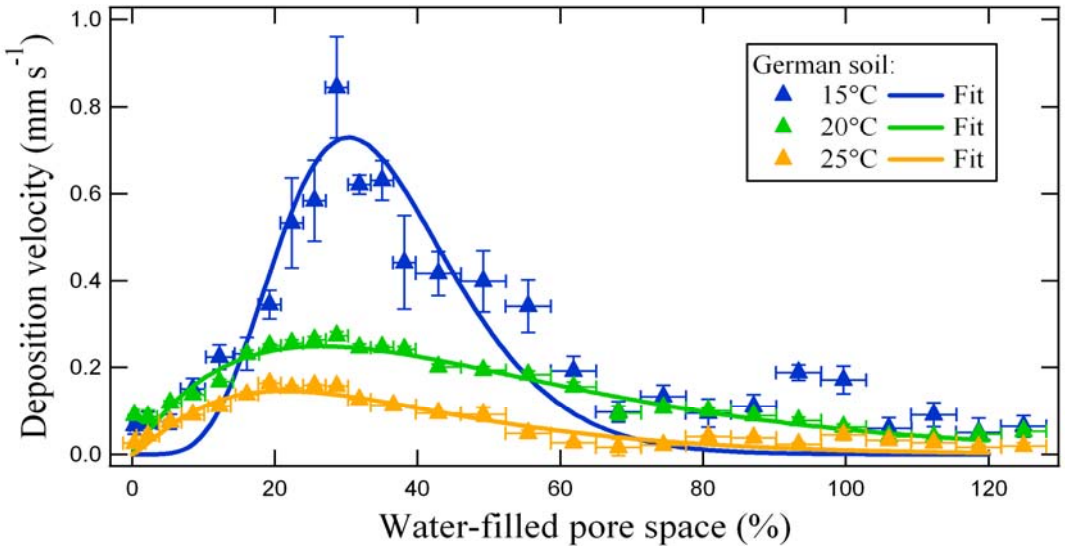

Figure 3.3: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to WFPS (%) for the German arable soil at 15°C, 20°C and 25°C. Each data point represents the mean value of at least 5 measurements with their standard errors.

3.1.3. Temperature dependence

Figure 3.4 shows the normalized V_d data in relation to the temperature regimes at 11.5% WC.

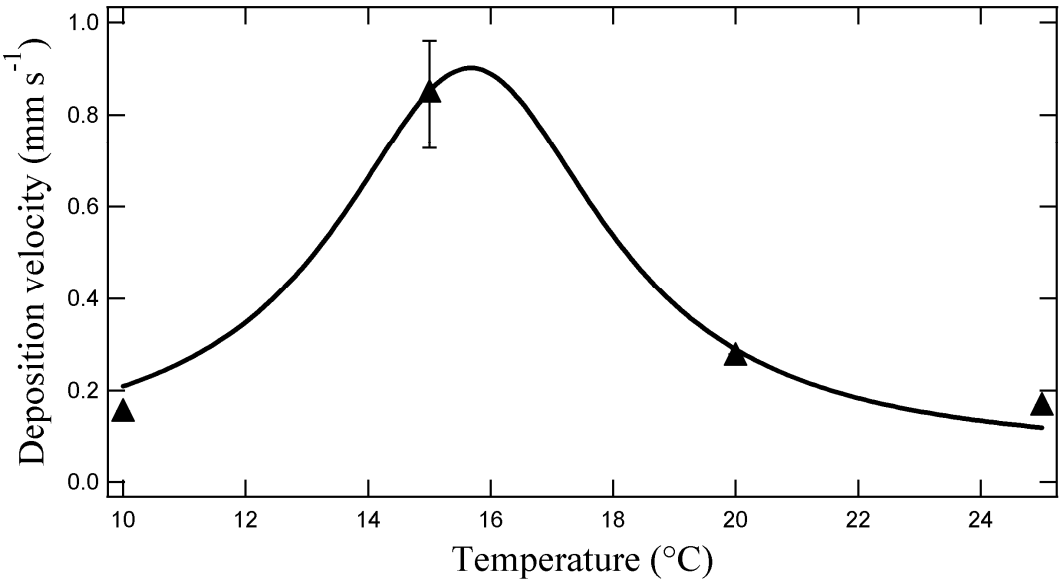

Figure 3.4: Normalized deposition velocity data (V_d; mm s^{-1}) for the German soil in relation to incubation temperatures between 10 and 25°C at their optimal soil WC. Some error bars were smaller than the symbol ($n \geq 5$; error bars are $\sigma/\sqrt{n}$). The data was plotted according to Meixner and Yang (2006) (see 2.4.2.).

The V_d increased with temperature up to an optimum between 15 and 17°C, followed by a decrease at higher temperatures. The temperatures shown represent the incubation temperatures (see 2.3.3.).

3.2. Chinese soil

3.2.1. COS V_d versus WC and WFPS at different temperatures

The Chinese soil, a sandy arable soil from an arid region in the temperate zone of Northeast of China, had a totally different structure and therefore a much lower field capacity (Table 3.2).

Table 3.2: Chemical and physical characteristics for the Chinese arable soil.

Properties	Chinese soil
C_{total}, wt%	0.40
S_{total}, wt%	0.030
N_{total}, wt%	0.040
Field capacity, % H_2Og^{-1} DW	32.7
Bulk density, g cm^{-3}	1.40
Calculated maximum WFPS, %	69.28
pH at 25°C	7.28

Furthermore, calculated V_ds for this soil exhibited a clear and sharp optimum at lower soil WC (9%) and at a higher optimum temperature (30°C) (Figure 3.5). In general, this soil exhibited V_ds in the range of 0.5 and 0.9 mm s^{-1} at temperatures between 25 – 30°C and soil WCs between 7 and 11%.

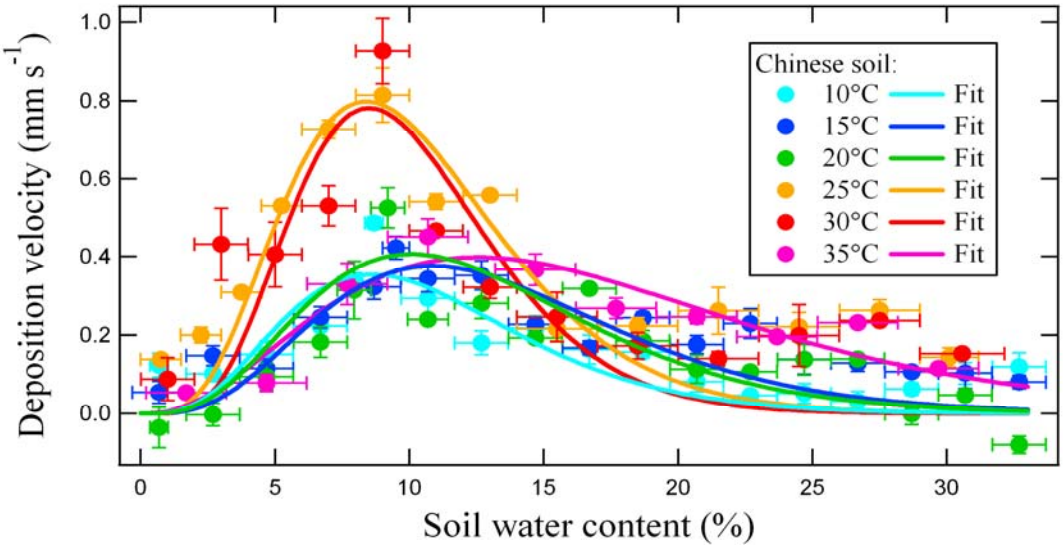

Figure 3.5: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to soil WC (%) for the Chinese sandy soil at 10°C, 15°C, 20°C, 25°C, 30°C and 35°C. Each data point represents the mean value of at least 3 measurements with their standard errors.

The V_d for the Chinese sandy soil in relation to WFPS showed an optimum near 19% WFPS (Figure 3.6).

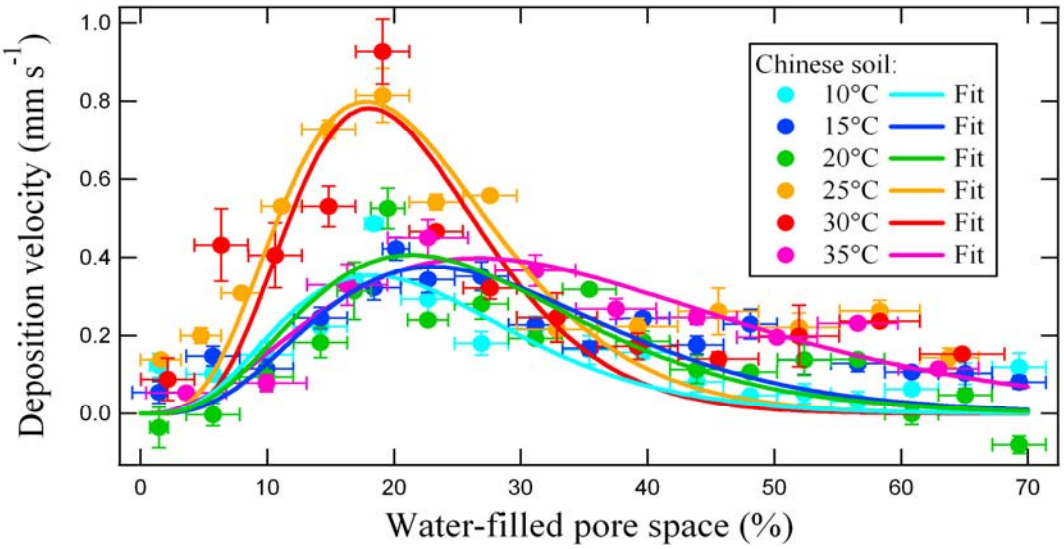

Figure 3.6: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to WFPS (%) for the Chinese sandy soil at 10°C, 15°C, 20°C, 25°C, 30°C and 35°C. Each data point represents the mean value of at least 3 measurements with their standard errors.

The incubation times for the Chinese arable soils were 3239 min, 2379 min, 2373 min, 1129 min, 997 min and 698 min for 10°C, 15°C, 20°C, 25°C, 30°C and 35°C, respectively.

3.2.2. Temperature dependence

Figure 3.7 shows the normalized V_d data in relation to the temperature regimes at 9% soil WC. The V_d increased with temperature up to an optimum between 25 and 32°C, followed by a sudden decrease at higher temperatures. The temperatures shown in figure 3.7 represent the incubation temperatures.

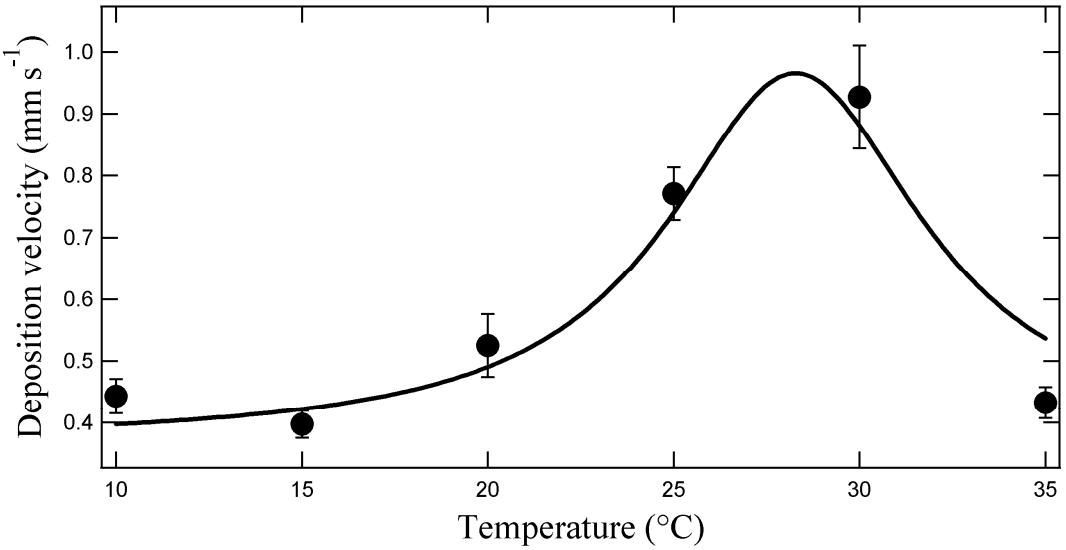

Figure 3.7: Normalized deposition velocity data (V_d; mm s^{-1}) for the Chinese soil in relation to incubation temperatures between 10 and 35°C at their optimal soil WC. Some error bars were smaller than the symbol (n ≥ 3; error bars are σ/√n). The data were plotted according to Meixner and Yang (2006).

3.3. Finnish soil

This Finnish arable soil had a moraine origin with a relatively coarse texture and a mean particle size at about 0.1 mm. Compared to the German soil, this soil had approximately the same field capacity and a comparable soil pH. Despite of the slightly elevated total S (wt %) value, all other measurable chemical features (C_{total} (wt %) and N_{total} (wt %)) were approximately the same (Table 3.3).

Table 3.3: Chemical and physical characteristics for the Finnish arable soil.

Properties	Finnish soil
C_{total}, wt%	2.42/2.18
S_{total}, wt%	0.08/0.04
N_{total}, wt%	0.16/0.14
Field capacity, % H_2Og^{-1} DW	42.68
Bulk density, g cm^{-3}	1.08
Calculated maximum WFPS, %	72.03
pH at 25°C	7.83

3.3.1. COS V_d versus WC and WFPS at different temperatures

In contrary to the German soil which had its optimum V_d around 15°C, the Finnish soil exhibited a V_d optimum in the range of 25 – 30°C (Figure 3.8). Soil WCs between 7 and 20% resulted in a maximum of COS uptake at 25°C, but further increases in the soil WC led to a decrease in exchange, although the exchange was still high compared with other soils. Temperatures which were lower than 20°C led to a clear decline in COS exchange.

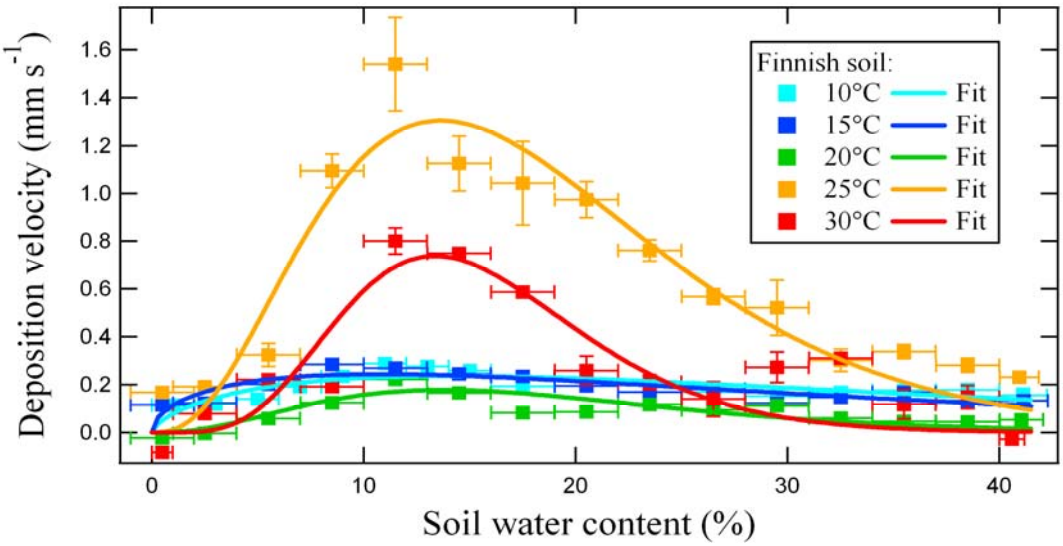

Figure 3.8: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to soil WC (%) for the Finnish soil at 10°C, 15°C, 20°C, 25°C, and 30°C. An optimum exchange was reached at 25°C and 11.5% WC. Each data point represents the mean value of at least 3 measurements with their standard errors.

WFPS was calculated according to the soils bulk density, which was typical for each soil. Again it was obvious that soil structure as well as soil WC and temperature were important factors to parameterize the COS exchange of different soils around the world. The Finnish soil also exhibited an optimum uptake near 19% WFPS (Figure 3.9).

The incubation times for the Finnish arable soils were 4691 min, 3099 min, 2151 min, 1614 min and 1330 min at 10°C, 15°C, 20°C, 25°C and 30°C, respectively.

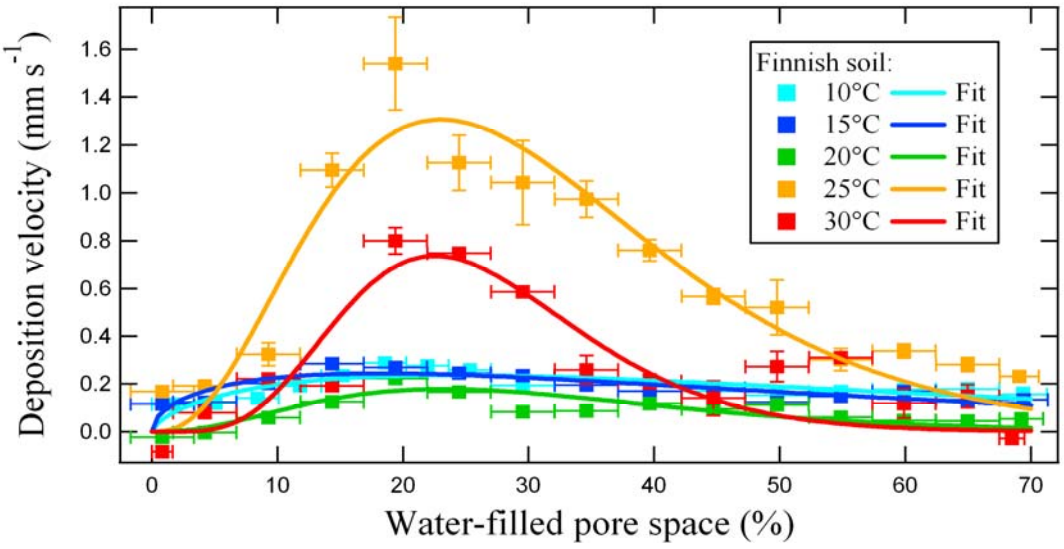

Figure 3.9: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to WFPS (%) for the Finnish soil at 10°C, 15°C, 20°C, 25°C, and 30°C. An optimum exchange was reached near 19% WFPS. Each data point represents the mean value of at least 3 measurements with their standard errors.

3.3.2. Comparison of the Finnish and Chinese arable soil

Comparison of the optima of the V_d of the Chinese and Finnish soil in relation to soil WC at their optimal temperatures of 30°C and 25°C, respectively, showed clearly separated peaks of activities (Figure 3.10).

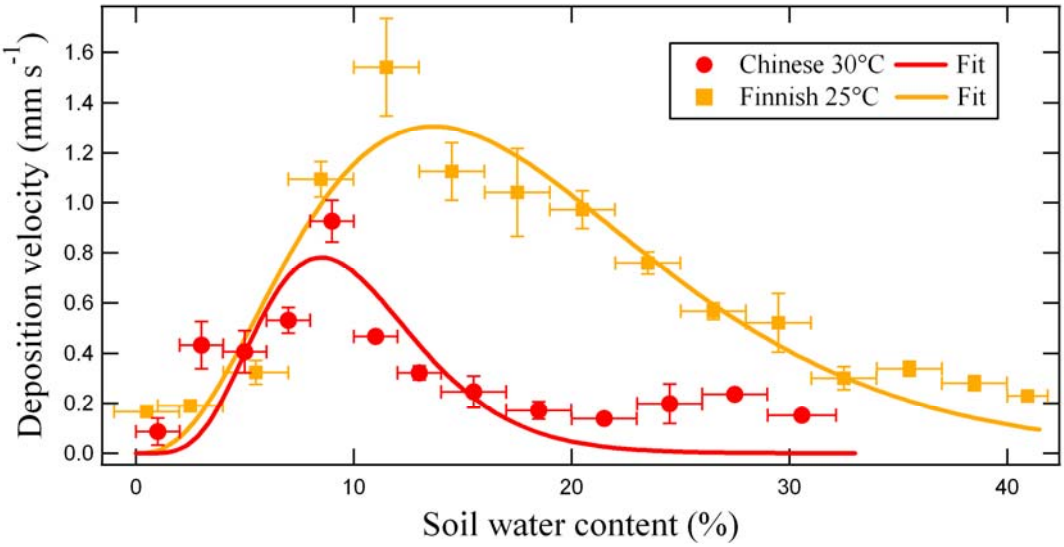

Figure 3.10: Deposition velocity (V_d; mm s^{-1}) optima for the Finnish and Chinese soil both at their optimal temperatures of 25°C and 30°C, respectively, in relation to the soil WC (%).Some error bars were smaller than the symbol ($n \geq 3$; error bars are $\sigma/\sqrt{n}$).

As already mentioned in section 3.3.1, the optimum V_d was found near 19% WFPS, which was also the case for the Chinese arable soil at its optimal temperature but at a much lower uptake level.

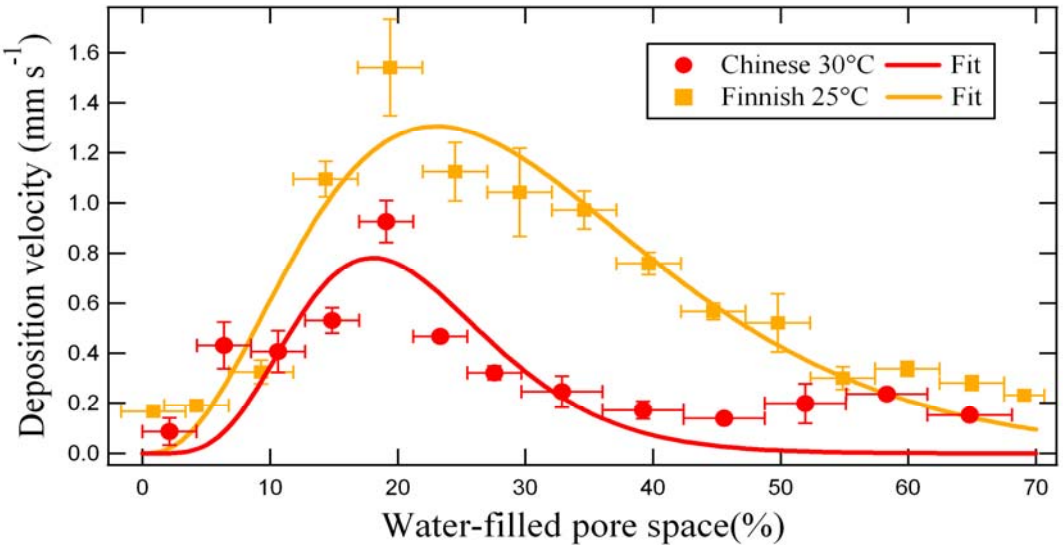

Figure 3.11: Deposition velocity (V_d; mm s^{-1}) optima for the Finnish and Chinese soil both at their optimal temperatures coincide near 19% WFPS. Some error bars were smaller than the symbol ($n \geq 3$; error bars are $\sigma/\sqrt{n}$).

The result indicates that soil structure and physical gas diffusion play an important dominating role for the COS uptake by soil. Furthermore, comparison of the two soils in relation to the WFPS especially highlighted the difference in the quantity of the COS uptake (Figure 3.11). The maximum V_d for the Finnish soil was twice as high as the maximum V_d for the Chinese soil at their optimal temperature of 25°C and 30°C, respectively.

3.3.3. Temperature dependence

Figure 3.12 shows the normalized V_d data in relation to the temperature regimes at 11.5% soil WC. The V_d increased with temperature up to an optimum around 25°C, followed by a sharp decrease at higher temperatures. As for the other soils, temperatures shown in figure 3.12, represent the incubation temperatures.

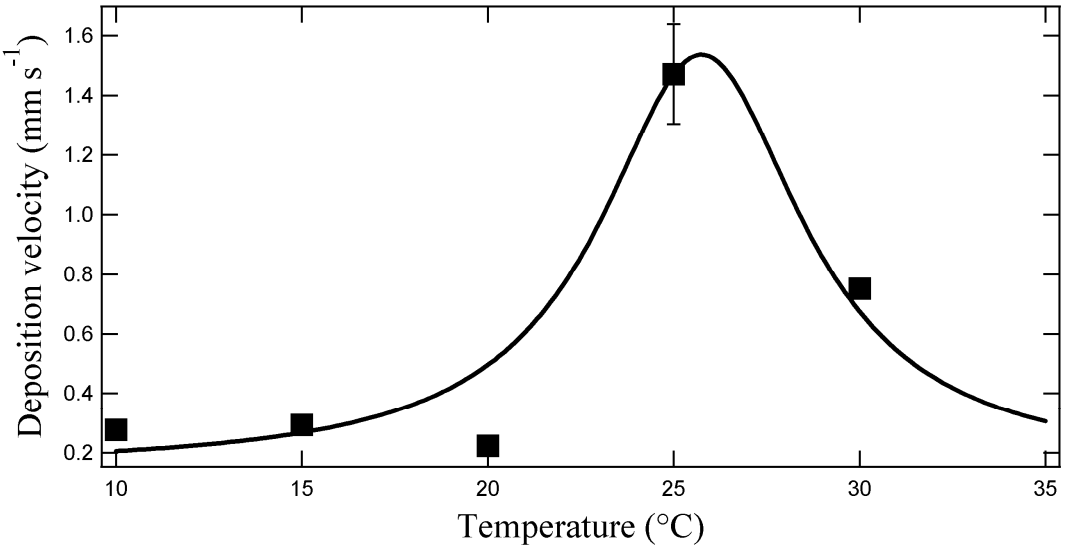

Figure 3.12: Normalized deposition velocity data (V_d; mm s^{-1}) for the Finnish soil in relation to incubation temperatures between 10 and 30°C at their optimal soil WC. Some error bars were smaller than the symbol (n ≥ 3; error bars are σ/√n). The data were plotted according to Meixner and Yang (2006).

3.4. Siberian soil

This sandy soil came from a boreal forest in Zotino along 60° N. The soil had a podzolic origin and was therefore characterized by a low pH (Table 3.4). The chemical measurable characteristics, C_{total} (wt %), S_{total} (wt %) and N_{total} (wt %), were rather low as also observed for the Chinese soil.

Table 3.4: Chemical and physical characteristics for the Siberian forest soil.

Properties	Siberian soil
C_{total}, wt%	0.37/0.39
S_{total}, wt%	0.02/0.04
N_{total}, wt%	0.02/0.03
Field capacity, % H_2Og^{-1} DW	29.30
Bulk density, g cm^{-3}	1.43
Calculated maximum WFPS, %	63.64
pH at 25°C	4.20

3.4.1. COS V_d versus WC and WFPS at different temperatures

The highest V_ds were reached at temperatures between 25 and 30°C, lower temperatures led to a clear decline in COS exchange. In terms of soil WC, maximum V_ds were found at a rather low soil WC of 9%, but deposition velocities were still high between 7 and 11% of soil WC (Figure 3.13). Although, this soil originated from a forest instead of an agriculture site, it still exhibited the same exchange pattern when compared to the German, Chinese and Finnish soil.

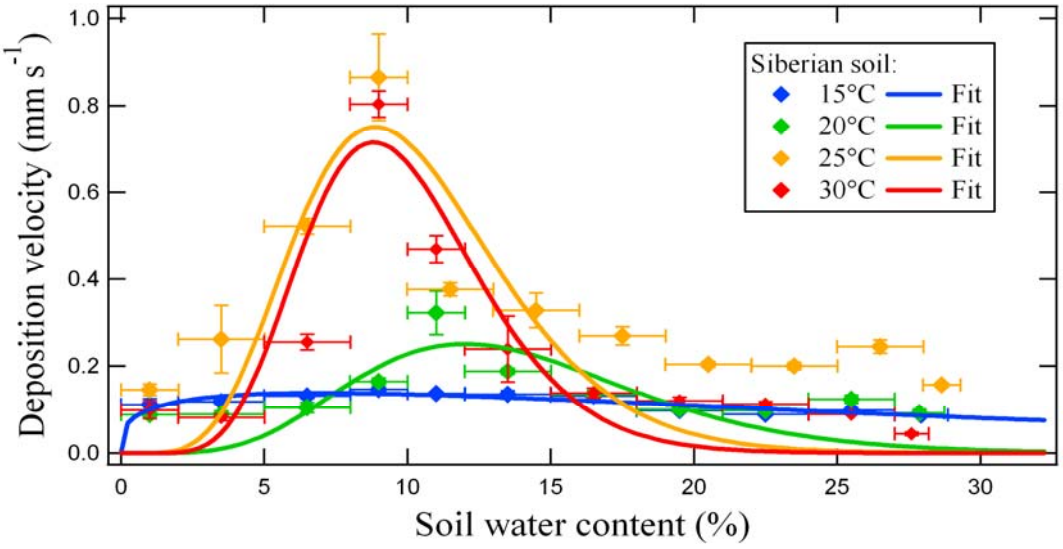

Figure 3.13: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to soil WC (%) for the Siberian forest soil at 15°C, 20°C, 25°C, and 30°C. An optimum exchange was reached at 25°C and 9% WC. Each data point represents the mean value of at least 3 measurements with their standard errors.

The V_d for the Siberian soil in relation to WFPS showed an optimum near 19% WFPS as well (Figure 3.14).

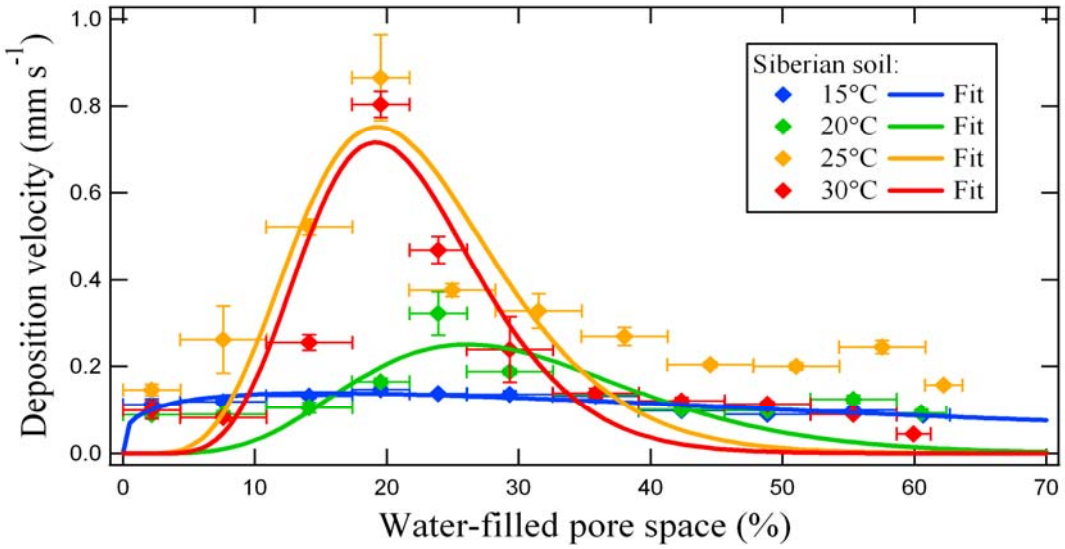

Figure 3.14: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to WFPS (%) for the Siberian forest soil between 15°C and 30°C. An optimum exchange was reached near 19% WFPS. Each data point represents the mean value of at least 3 measurements with their standard errors.

3.4.2. Comparison of the Siberian and Chinese soil

The Siberian soil represented one of the world's forest soils. However, in comparison with the Chinese and Finnish arable soils, V_ds in relation to WFPS exhibited an optimum at similar WFPS.

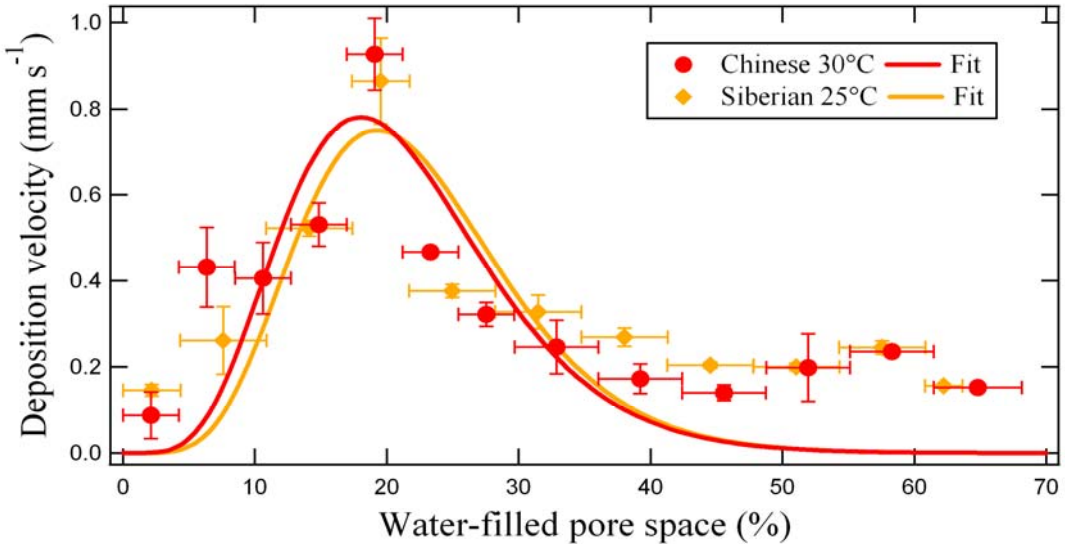

Figure 3.15: V_d (mm s^{-1}) optima for both soils coincide around 19% WFPS for both soils at optimum temperatures. Some error bars were smaller than the symbol (n ≥ 3; error bars are σ/√n).

Furthermore, in comparison with the Chinese arable soil, maximum V_ds in relation to WFPS were found in the same range of 0.8 – 0.9 mm s^{-1} at its optimum temperature and around 19% WFPS (Figure 3.15).

3.4.3. Temperature dependence

Figure 3.16 shows the normalized V_d data in relation to the temperature regimes at 9% soil WC. The V_d increased with temperature up to an optimum between 25 and 30°C, followed by a decrease at higher temperatures. As for the arable soils, temperatures shown in figure 3.16, represent the incubation temperatures.

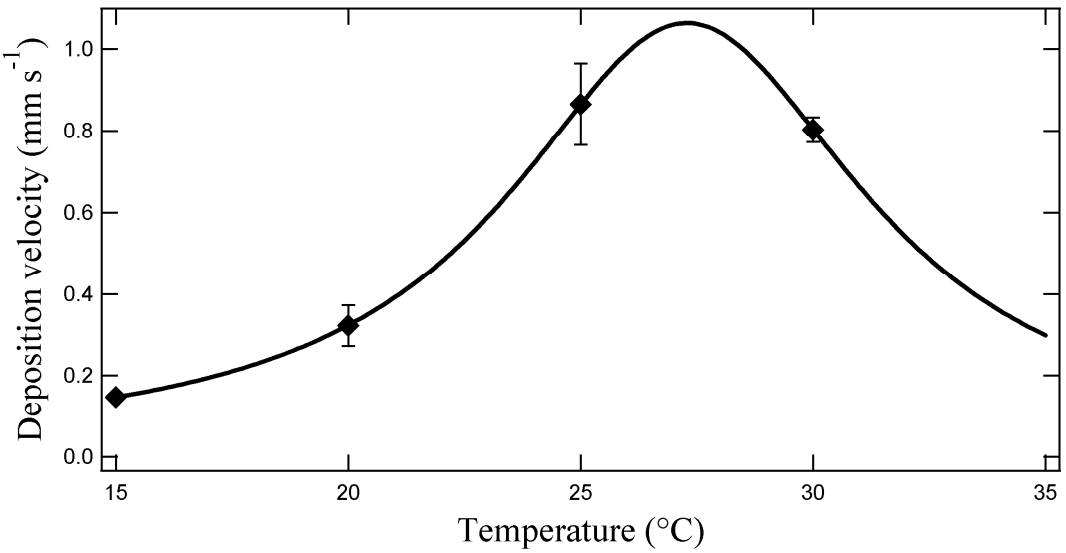

Figure 3.16: Normalized deposition velocity data (V_d; mm s^{-1}) for the Siberian forest soil in relation to incubation temperatures between 15 and 30°C at their optimal soil WC. Some error bars were smaller than the symbol (n ≥ 3; error bars are σ/√n). The plotted line represents the mathematical approximation (Meixner and Yang, 2006).

3.5. Surinam soil

Since it was important to measure soils from all over the world, a soil from a tropical region (Surinam, South America) was also investigated. The soil originates from a lowland forest region, which is typical for tropical areas. It was noteworthy that this soil had the highest values for C_{total} (wt %), S_{total} (wt %) and N_{total} (wt %), but a much lower pH (Table 3.5).

Table 3.5: Chemical and physical characteristics for the forest soil from Surinam.

Properties	Surinam soil
C_{total}, wt%	2.69/2.61
S_{total}, wt%	0.09/0.12
N_{total}, wt%	0.20/0.18
Field capacity, % H_2Og^{-1} DW	42.5
Bulk density, g cm^{-3}	0.78
Calculated maximum WFPS, %	60.22
pH at 25°C	4.13

3.5.1. COS V_d versus WC, WFPS and different temperatures

Despite of the fact that the Siberian soil is a forest soil, it was found to act in the same way as the arable soils. However, the Surinam tropical forest soil exhibited V_ds at different soil WCs at all temperatures (Figure 3.17). Because of technical problems during the incubation series at 10°C, we lost some data between 5 and 15% soil WC.

Even after calculation soil WFPS, the Surinam soil exhibited an irregular pattern (Figure 3.18). Therefore, it was not possible to compare this soil with the other soils, either to use the algorithm of Meixner and Yang (2006).

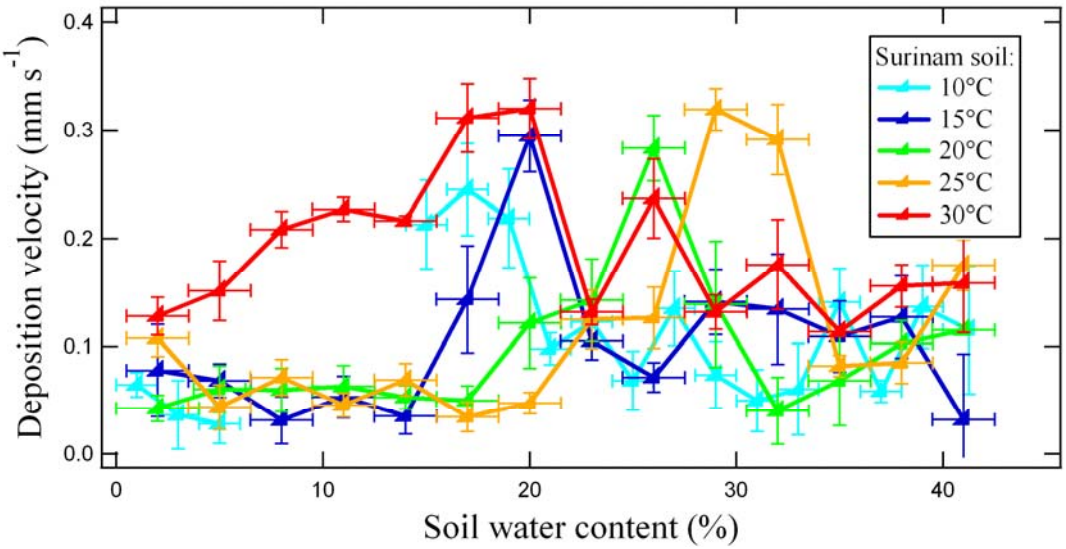

Figure 3.17: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to soil WC (%) for the Surinam soil at 10°C, 15°C, 20°C, 25°C, and 30°C. An optimum exchange could not be related to soil WCs. Each data point represents the mean value of at least 3 measurements with their standard errors.

A closer look on figure 3.18 revealed that V_d optima related to WFPS shifted with changing temperatures. The optima increased from 25% WFPS to more than 40% under temperatures from 10°C to 25°C but then dropped to 25% again at 30°C.

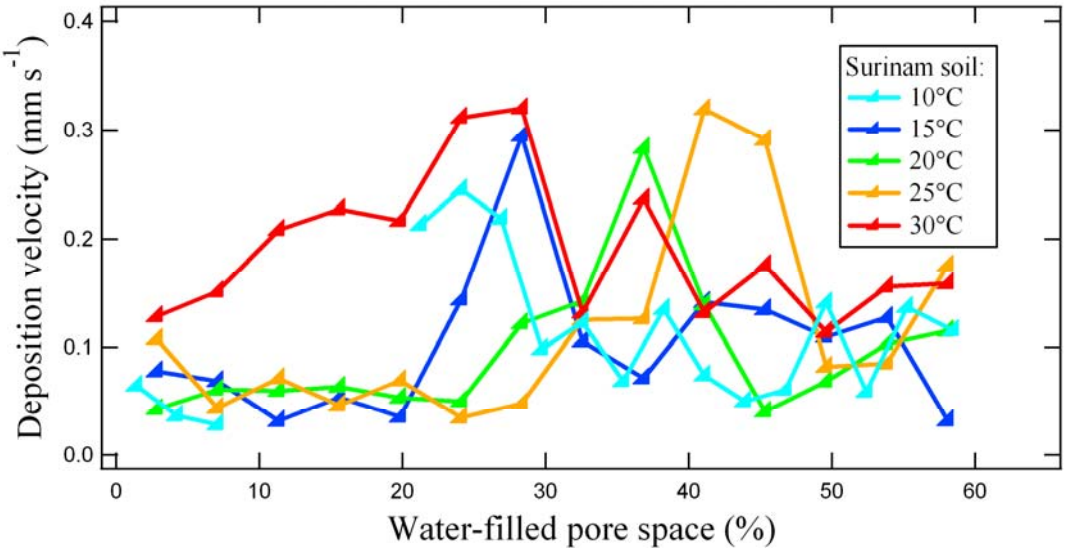

Figure 3.18: Deposition velocities (V_d; mm s^{-1}; normalized uptake rates) in relation to WFPS (%) for the Surinam forest soil at 10°C, 15°C, 20°C, 25°C, and 30°C. An optimum exchange could not be related to WFPS. Each data point represents the mean value of at least 3 measurements.

3.6. Comparison of the German, Chinese, Finnish and Siberian soil

3.6.1. Comparison in relation to soil WC and WFPS

It was worthwhile to compare the exchange patterns of all soils at their optimum temperature. Since the forest soil from Surinam exhibited a completely different exchange pattern for COS, this soil was not taken into account.

The COS V_ds showed a clear optimum around a low soil WC of ~11.5%, ~9%, ~9% and ~11.5% for the German, Chinese, Siberian and Finish soil, respectively (Figure 3.19).

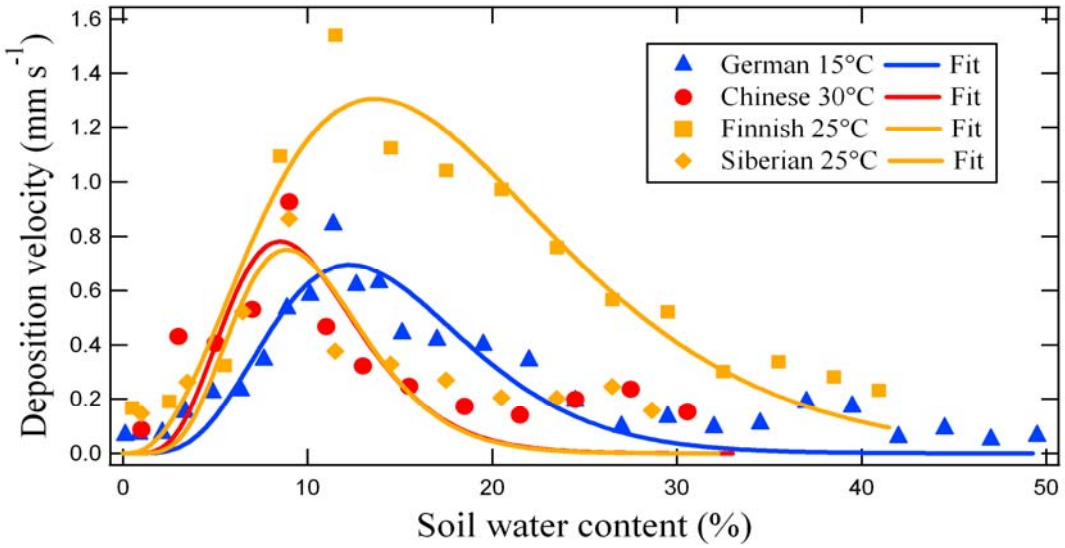

Figure 3.19: Comparison of the V_d for the four different soils at the optimal temperatures with maximum COS uptake in relation to the soil WC. Each data point represents the mean value of at least 3 measurements.

The distinct behavior of those four soils gave reason to assume a strong adaptation of gas exchange to different soil types. An overview is given in table 3.6.

Table 3.6: An overview of the optimum V_d, optimum temperature, optimum soil WC and WFPS is given for the German, Chinese, Finnish and Siberian soils.

	German soil	Chinese soil	Finnish soil	Siberian soil
V_d at optimum soil WC and temperature ± standard error [mm s^{-1}]	0.844 ± 0.099	0.927 ± 0.083	1.541 ± 0.194	0.865 ± 0.099
Optimum temperature [°C]	15	30	25	25
Optimum soil WC [%]	11.5	9	11.5	9
Optimum WFPS [%]	29	19	19	19

Surprisingly, COS V_ds related to the WFPS instead of the soil WC exhibited a comparable exchange pattern for all soil types indicating that soil texture in relation to soil WC was the

dominating factor. The German soil exhibited a maximum V_d at a different optimum temperature and WFPS. Optima for the Chinese, Finnish and Siberian soils coincided at around 19% WFPS (Figure 3.20). Since those three soils originate from boreal regions, we will further describe them as boreal soils.

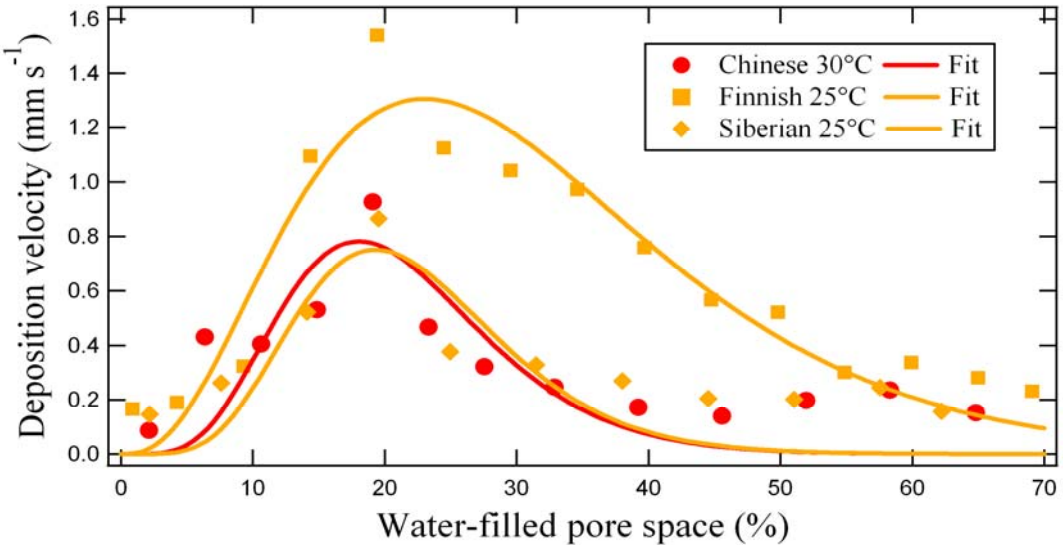

Figure 3.20: COS V_d (mm s^{-1}) for the Chinese, Finnish and Siberian soil related to the WFPS. Optima for those boreal soils coincided around 19% WFPS. Each data point represents the mean value of at least 3 measurements.

3.6.2. Comparison in relation to temperature

Figure 3.21 shows the normalized V_d data for the German, Chinese, Finnish and Siberian soil in relation to the temperature regimes at 11.5%, 9%, 11.5% and 9% soil WC, respectively. The V_d increased with temperature up to an optimum between 15 and 17°C for the German soil, followed by a decrease at higher temperatures. In contrast, V_d optima for the boreal soils were found at higher temperatures between 25 and 30°C. As mentioned before, the temperatures shown represent the incubation temperatures. It is of interest to see more soils to exhibit high temperature optima.

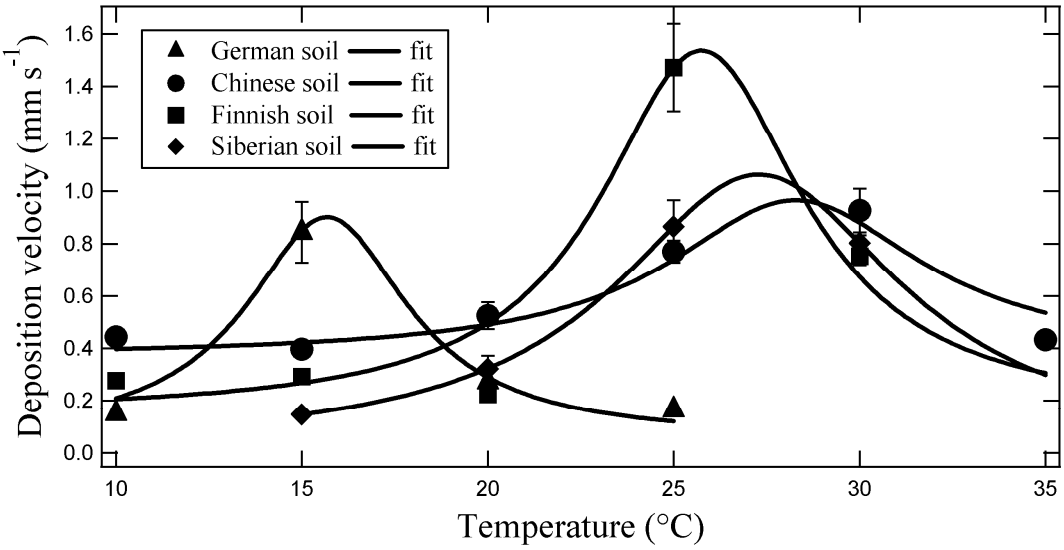

Figure 3.21: Normalized deposition velocity data (V_d; mm s^{-1}) for the German, Chinese, Finnish and Siberian soil in relation to incubation temperatures between 10 and 35°C. All data are given for their optimal soil WC. Some error bars were smaller than the symbol with ($n \geq 3$; error bars are $\sigma/\sqrt{n}$). The plotted line represents the mathematical approximation (Meixner and Yang, 2006).

3.7. Enzymatic activity of CA in soils

Since carbonic anhydrase (CA) was determined as the key enzyme for the uptake of COS by soils, CA-activity was investigated for all 5 soils using a modified method of Wilbur and Anderson (1948) (see 2.5). This method is based on the pH-drop caused by the reaction between H_2O and CO_2, catalyzed by CA. Enzyme units are calculated from the time the catalyzed and non-catalyzed reactions need to drop the pH from pH 8.2 to 7.7.

All soils were treated in the same way and seemed to show a distinct activity, CA-activity data was still very scattered for each soil. Therefore, these results have to be considered as very preliminary.

3.7.1. German soil

Figure 3.22 represents 2 pairs of measurements from table 3.1 of pH-drop for the catalyzed (German soil sample 1 and 2) and the non-catalyzed (Reference 1 and 2) reactions.

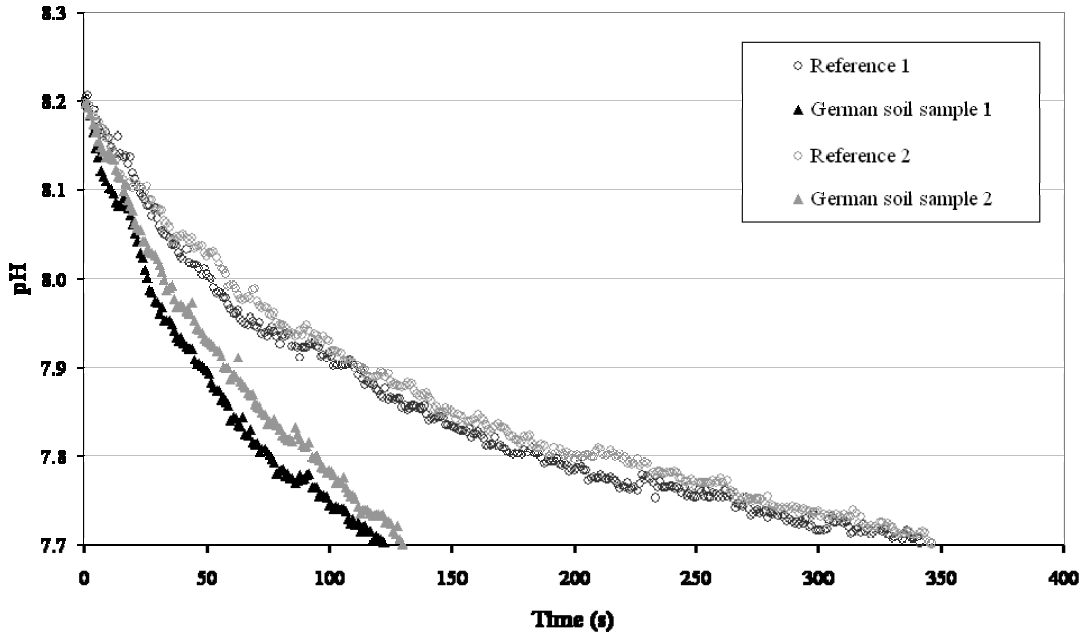

Figure 3.22: pH-drop for 2 pairs of measurements for the non-catalyzed (Reference 1 and 2) and the catalyzed reaction (German soil sample 1 and 2). The CA-activity was calculated with T_0 (the time in which the pH drops with 0.5 in the non-catalyzed reaction) and T_e (the time in which the pH drops with 0.5 in the catalyzed reaction).

The enzymatic activity (units) was calculated from the time the catalyzed and non-catalyzed reactions need to drop the pH from pH 8.2 to 7.7. Table 3.7 presents the preliminary CA-activity measured in the summer of 2006 for the German soil. Besides the CA-activity, the median, the 25% percentile and the 75% percentile are also given.

Table 3.7: Enzymatic activity of CA for the German soil (n = 15).

T_0	T_e	CA-activity (units)	Median	25% percentile	75% percentile
341	122	1.80	0.29	0.17	0.53
417	383	0.09			
396	298	0.33			
404	341	0.18			
312	268	0.16			
312	282	0.11			
256	277	0.29			
515	379	0.36			
346	130	1.66			
340	288	0.18			
266	186	0.43			
270	253	0.07			
200	163	0.23			
289	178	0.62			
213	120	0.78			

3.7.2. Chinese soil

Figure 3.23 represents 2 pairs of measurements from table 3.8 of pH-drop for the catalyzed (Chinese soil sample 1 and 2) and the non-catalyzed (Reference 1 and 2) reactions. These pairs of measurements present data where the time difference between T_0 and T_e was less pronounced. Nevertheless, figure 3.23 was displayed to show the different results, even when the same procedure was performed.

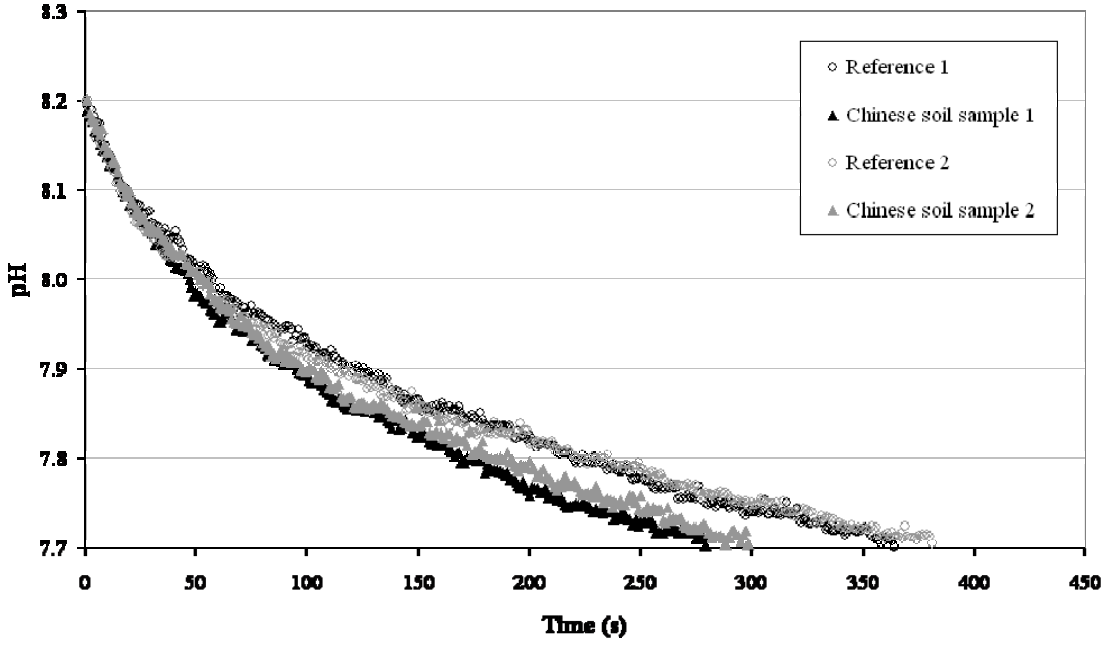

Figure 3.23: pH-drop for 2 pairs of measurements for the non-catalyzed (Ref 1 and 2) and the catalyzed reaction (Chinese soil sample 1 and 2). The CA-activity was calculated with T_0 and T_e.

Table 3.8: Enzymatic activity of CA for the Chinese soil (n = 14).

T_0	T_e	CA-activity (units)	Median	25% percentile	75% percentile
350	308	0.14	0.24	0.14	0.37
381	298	0.28			
383	202	0.90			
266	214	0.24			
332	187	0.78			
373	136	1.74			
367	324	0.13			
332	324	0.02			
306	296	0.03			
362	291	0.24			
311	267	0.16			
402	290	0.39			
492	367	0.34			
301	246	0.22			

Table 3.8 presents the preliminary CA-activity measured in the summer of 2006 for the Chinese soil. Besides the CA-activity, the median, the 25% percentile and the 75% percentile are also given.

3.7.3. Finnish soil

The Finnish soil exhibited similar values for the CA-activity as found for the other soils. Table 3.9 shows the measured values of T_0 and T_e together with the calculated CA-activity.

Table 3.9: Enzymatic activity of CA for the Finnish soil (n = 8).

T_0	T_e	CA-activity (units)	Median	25% percentile	75% percentile
360	248	0.45	0.35	0.28	0.37
468	338	0.38			
348	290	0.20			
322	251	0.28			
254	187	0.36			
422	313	0.35			
284	223	0.27			
326	238	0.37			

3.7.4. Siberian soil

Also the Siberian forest soil exhibited comparable values of the CA-activity. Table 3.10 shows all values with the median, the 25% and 75% percentile.

Table 3.10: Enzymatic activity of CA for the Siberian forest soil (n = 21).

T_0	T_e	CA-activity (units)	Median	25% percentile	75% percentile
357	285	0.25	0.25	0.20	0.75
431	362	0.19			
291	188	0.55			
508	187	1.72			
316	240	0.32			
541	450	0.20			
404	231	0.75			
410	342	0.20			
369	324	0.14			
371	291	0.27			
305	150	1.03			
337	242	0.39			
424	390	0.09			
280	159	0.76			
259	152	0.70			
265	138	0.92			
406	200	1.03			
376	328	0.15			
342	277	0.23			
355	276	0.29			
404	356	0.13			

3.7.5. Surinam soil

As far as the CA-activity is concerned, the Surinam soil exhibited a significantly higher CA-activity compared to all other soils (Table 3.11).

Table 3.11: Enzymatic activity of CA for the Surinam soil (n = 11).

T_0	T_e	CA-activity (units)	Median	25% percentile	75% percentile
275	201	0.37	0.68	0.37	1.10
338	174	0.94			
361	246	0.47			
291	129	1.26			
318	189	0.68			
308	135	1.28			
248	182	0.36			
330	170	0.94			
236	191	0.24			
379	153	1.48			
290	235	0.23			

4. Discussion

The obtained experimental results confirm that soil is a significant sink for COS (Kesselmeier *et al.*, 1999; Kuhn *et al.*, 1999). High time resolution measurements with a fully automatic instrument allowed a more exact statistical approach. The close accordance of this repetition with those 5 years old findings by Kesselmeier *et al.* (1999) on the same German arable soil (same site) demonstrates the reproducibility of such measurement techniques as well as the constant characteristics of soils. Although, this soil was yearly used for agriculture purposes and the soil was tilled by the farmers.

To our knowledge, this was the first time that 5 totally different soil types around the world were parameterized and directly compared. These experiments were performed in order to get a better understanding about COS exchange between soils and the atmosphere on a global scale.

4.1. General findings

All soils were measured under the same controlled parameters in order to get information about the relations between uptake rates and environmental parameters, such as soil water content (WC) and water filled pore space (WFPS) related to soil structure and the number of pores and temperature. In addition enzymatic activity was investigated with a modified method of Wilbur and Anderson (1948).

4.2. German soil

4.2.1. Comparison with literature: Teusch (1998) and Kesselmeier *et al.*(1999)

Teusch (1998) and Kesselmeier *et al.* (1999) found a linear correlation of COS exchange and soil mass up to 200g soil per cuvette and shifted to a saturation-like exchange behavior with increasing soil masses between 200 and 400g of soil. For this finding, Teusch (1998) measured the COS uptake of the German arable soil for different soil masses between 50 and 400g and found a correlation between COS uptake and soil mass, which was mathematically supported by the following equation.

$$y = 2 \cdot 10^{-5} x^2 + 0.0158x \quad [12]$$

With y: soil mass (g)
x: COS-uptake (pmol cm^{-2} h^{-1})

Assuming that the linear correlation between the COS uptake and the soil mass up to 200g still accounts for the German soil five years later, we were able to recalculate our data to 80g of soil per cuvette. Thus, measurements of the German arable soil could be compared with the data of the other soils measured.

The German arable soil, consisting of sandy clay with low loess content, was re-investigated for its exchange capacity with the atmosphere. In order to compare our data with those of Teusch (1998) the experiments of the German soil were performed for 200g of soil. Uptake rates measured by Teusch (1998) are recalculated to deposition velocities (V_d) at 200g of soil to eliminate the influence of the fluctuations of COS mixing ratio's. Table 4.1 compares some of the maximum V_d at similar optimum soil WC and temperature.

Table 4.1: Comparison of maximum V_d in this study with Teusch (1998) at similar optimum soil WC and temperature.

Teusch (1998)			**This study**		
V_d at 200g [mm s^{-1}]	**Soil WC [%]**	**Temperature [°C]**	**V_d at 200g [mm s^{-1}]**	**Soil WC [%]**	**Temperature [°C]**
0.423	10.17	15.96	1.742	10.43	15.69
0.398	10.19	15.96	2.041	10.05	15.66
0.412	10.22	15.78			
Average V_d: 0.411 mm s^{-1}			**Average V_d: 1.891 mm s^{-1}**		
Factor of 4.6 of difference					

It is obvious that the deposition velocities measured by Teusch (1998) are an order of magnitude (4.6) smaller than the V_d measured in this study which could be explained by the difference in experimental setup. Teusch (1998) measured the uptake rates of table 4.1 at a fixed soil WC by measuring at a relative humidity of 90%. Our data was obtained by drying out the soil from its maximum field capacity to 0% soil WC and therefore at a varying relative

humidity. The different method of cryogenic trapping might be also a possible explanation for the factor of 4.6 of difference in uptake. Teusch (1998) used a 20 cm long (glass) cryotrap filled with silinized glass wool and fluid argon (-186°C) to freeze the trap. The injection on the GC was initialized by warming the trap in water. In this study a fully automatic system (as described in 2.3.4.) was used.

Nevertheless, a comparable exchange pattern was found and maximum V_ds were found at similar optimum soil WCs (9 – 14%) and at an optimum temperature between 15 and 17°C, which demonstrates the accuracy of the data.

As already indicated by Teusch (1998), there is a fast increase in COS uptake at the low soil WC range until an optimum of 11.5% is reached. This could be explained by the increase of biochemical activity in the soil. According to Wilson and Griffith (1974) and Orchard and Cook (1983), the soil WC has a distinct influence on the movement and the metabolic activity of the soil microorganisms (Wilson and Griffith, 1974; Orchard and Cook, 1983). Thus, the movement and the nutrition of the soil bacteria will be rather limited when soil WC is low. Furthermore, the low water potentials have a direct influence on the enzymatic activity of microorganisms (Wilson and Harris, 1968). Moreover, the increase of COS deposition with increasing soil WC assumes an enzymatic background. After reaching the optimum soil WC of 11.5%, the sharp increase is followed by a sudden decrease of COS uptake, which could be attributed to a restricted diffusion.

Further experiments were performed with only 80g of soil to ensure the contribution of the entire soil mass in the exchange of COS and thus stay in the linear range between COS uptake and soil mass for all soils. Maximum deposition velocities (V_ds) for 80g of the German soil were found in the range of 0.7 – 0.9 mm s^{-1} at the optimum (measured) temperature of 15°C and a soil WC of 11.5%. The lower optimum temperature range was remarkable considering the optimum temperature for the Chinese, Finnish and Siberian soil. Lower and higher air temperatures envisaged a much lower uptake capability of COS by the German arable soil.

4.2.2. Comparison regarding soil structure

Soil structure and the number of pores are expected to have also a major influence on the diffusion and exchange of gases between soil and the atmosphere. The ratio of soil WC to total porosity of the soil, which is termed the WFPS, is commonly considered to be a suitable

expression of the soil WC, since WFPS is largely comparable among soils of different texture (Meixner and Yang, 2006). Therefore WFPS were calculated according to the typical bulk density (ρ_b) and a general particle density (ρ_S) of the soil (equation 2 and 3, chapter 2). The maximum V_d was reached near 29% WFPS, which is in reasonable agreement with Kesselmeier *et al.* (1999).

4.3. Comparison with other soils

The good resemblance of the measurements of the German soil with those of Kesselmeier *et al.* (1999) gave us a strong motivation to execute further experiments on other soil types around the world in order to parameterize and to compare the uptake of COS by different soils from different locations.

4.3.1. Chemical and physical characteristics

Differences in chemical characteristics (C_{total} (wt %), N_{total} (wt %) and S_{total} (wt %)) and physical characteristics (bulk density and pH) will be discussed in this section. The influence of temperature and soil WC (WFPS) will be discussed later on in more detail. An overview of all chemical and physical characteristics is given in table 3.1 until 3.5 (see Results, chapter 3). In this section, if not mentioned, all soils were compared with the German arable soil.

4.3.1.a. Soil chemical composition and pH

a) Finnish soil

Compared with the German soil the Finnish soil from moraine origin in the South of Finland near Hyytiälä represented the same values for N_{total} and C_{total}, but a 2 to 4 time higher value for the total S content of the soil. The pH was found to be 7.83 and could be considered as not significantly different from the German and Chinese soils.

b) Chinese and Siberian soil

The Chinese soil, a sandy arable soil from an arid region in the temperate zone of Northeast of China, had optically a totally different structure and therefore a much lower field capacity

(32.7%). The chemical composition of this sandy soil was found to be much different compared to the German soil. The total N and C content was even 3.75 and 5 times lower, respectively, in contrast with S_{total} which turned out to be comparable. The pH was found in the same range around pH 7.5 (at 25°C).

The Siberian soil originates from a boreal forest in the Zotino region along the 60° N instead from a agricultural site, but has the same chemical features as the Chinese soil. In contrast, the pH of this soil is very acid, this could be attributed to decomposed acid plant material. Figure 4.1 clearly demonstrates that pH seemed to have no influence on the COS exchange.

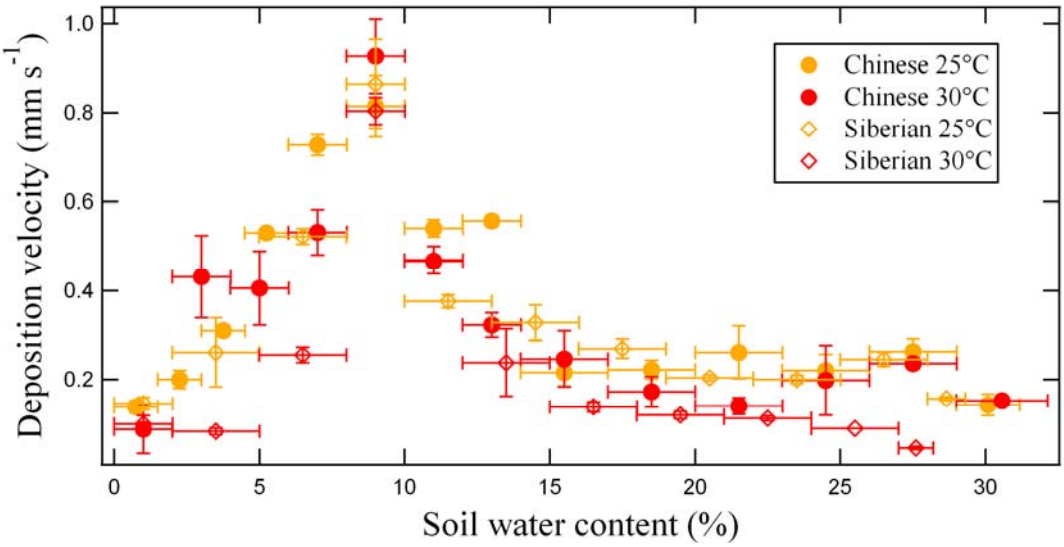

Figure 4.1: Comparison of V_d (mm s^{-1}) between the Chinese and Siberian soil in relation to the soil WC in order to demonstrate the similarity of the exchange pattern. Some error bars are smaller than the symbol (n ≥ 3; error bars are σ/√n).

c) Surinam soil

This tropical forest soil has a high total C and S content and a total N content which is comparable with the Chinese and Siberian soil. As for the Siberian forest soil, the soil pH was determined as acid in the pH range between 4 and 4.5. Since this soil exhibited a completely different exchange pattern, we did not compare this data with all other soils.

All soils turned out to be neutral or acidic, which excluded the possibility of cleavage of COS by chemical reactions (Dong *et al.*, 1998).

4.3.1.b. Bulk density and porosity

a) Chinese soil

The bulk density or the total mass of soil per unit of bulk volume was 1.40g cm^{-3} for the Chinese soil, which was 0.20g cm^{-3} lower compared to the German soil. Bulk density is often measured as an indicator of compaction and a basis for calculating porosity. This is the volume percentage of the total bulk of soil not occupied by solid particles and could be calculated from the volume of pores in a sample divided by the sample volume. Since we were not able to calculate porosity for our soils, we used the bulk density as indication for the importance of porosity in COS deposition.

b) Siberian soil

The bulk density of the Siberian soil was 1.43g cm^{-3} and thus approximately in the same range as the one of the Chinese soil. Even here, the similarities between the two soils were distinct.

c) Finnish soil

The bulk density of the Finnish soil was remarkably lower than those of the German, Chinese and Siberian soil. With a bulk density of only 1.08g cm^{-3}, the Finnish soil is supposed to have a higher porosity and should therefore have the biggest average pore size of all investigated soils and a better diffusivity.

Figure 3.19 clearly demonstrated that at its optimum temperature of 25°C and at its optimum soil WC of 11.5% the Finnish soil was found to exhibit a maximum V_d.
This was much higher than the maximum V_d at optimum conditions for all other soils. Therefore, we assumed that a lower bulk density (or higher porosity), which represented a better diffusivity, could play a major role in determining the amount of COS uptake.

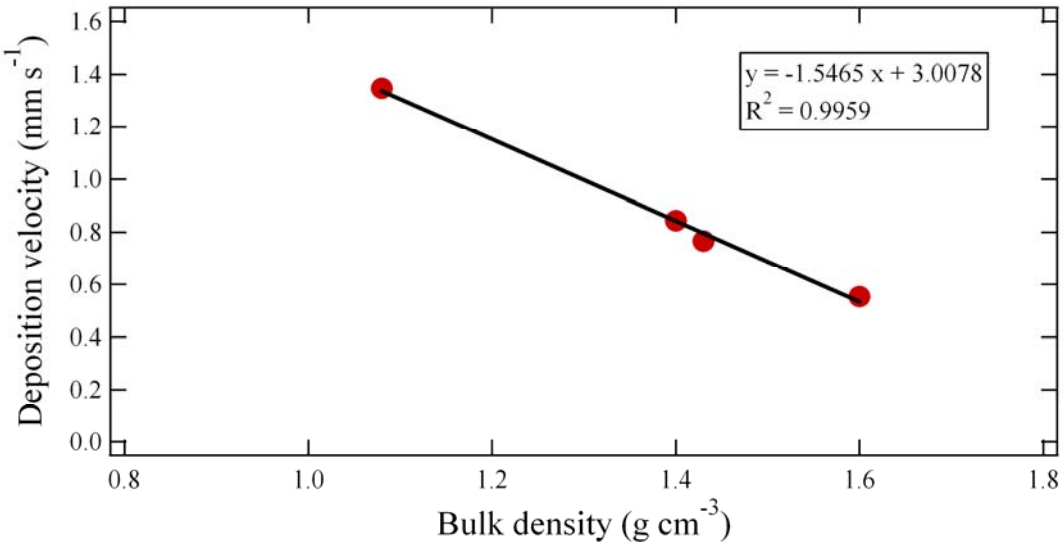

Figure 4.2: Maximum V_d (mm s^{-1}) of all soils at optimum conditions (optimum temperature, optimum soil WC) in relation to the measured bulk density (g cm^{-3}). From left to the right, data points are the maximum V_d of the Finnish, Chinese, Siberian and the German soil.

Figure 4.2 shows a convincing linearity between the maximum V_d of the Finnish, Chinese, Siberian and German soil, respectively, and the measured bulk density of each soil. The maximum V_d, indicated here, accounted for each soil at their individual optimum temperature, i.e. 15°C for the German soil, 25°C for the Finnish soil and Siberian soil, 30°C for the Chinese soil, and at their individual optimum soil WC, i.e. 11.5% for the Finnish and German soil, 9% for the Chinese and Siberian soil. Furthermore, optimum temperature and optimum soil WC are thought to be important for reaching the optimal enzymatic activity of carbonic anhydrase (CA), and thus, the enzymatic activity can not be taken as a measure for the higher maximum V_d of the Finnish soil. This gave us convincing evidence that diffusivity plays a key role in the quantity of COS uptake. Diffusivity is a limiting factor for COS uptake of soils with a low porosity and thus a higher bulk density and may play a more important key role than previously thought.

d) Surinam soil

Surprisingly this tropical soil had a much smaller bulk density of only 0.78g cm^{-3}, but this was not translated in a higher maximum V_d. Since the exchange pattern of this soil was completely different from all other soils, it was not supposed to have a direct influence on the linearity between maximum V_d and bulk density.

4.3.2. Uptake of COS under varying temperatures

It is obvious that temperature has a significant influence on several biological and biochemical processes, as temperature affects microbial activity and has been used in several laboratory studies to parameterize COS fluxes (Steinbacher *et al.*, 2004). The optimum curve in the dependence of COS uptake on temperature could be explained by an enzymatically catalyzed process, during which the enzymes amplify the trace gas exchange up to a certain threshold temperature. Above this temperature, the enzymes deteriorate and contribute less to the uptake. Kesselmeier *et al.* (1999) determined the COS uptake by the German arable soil under varying temperatures (0 – 30°C) as a function of COS mixing ratios between 0 and 1400 ppt and found a linear correlation between the exchange rates and COS mixing ratios under all investigated temperature regimes. In this study, measurements of COS uptake for all soils were performed under a constant temperature, but experiments for the same soil type were repeated for temperature between 10°C and 35°C. This data was used to describe the dependence of COS uptake on temperature under ambient conditions. Figure 3.21 showed the V_ds (mm s^{-1}) for the German, Chinese, Finnish and Siberian soil in relation to incubation temperatures between 10 and 35°C. All four soils pursued a similar exchange pattern. The uptake increased with temperature up to an optimum between a certain temperature range, followed by a sharp decrease at higher temperatures. Three of the soil types (Chinese, Finnish and Siberian soil) exhibited a maximum V_d in a range between 25 and 30°C, surprisingly this was not the case for the German soil which originates from a more temperate climate. The optimum temperature for the German arable soil was found between 15 and 17°C. Nevertheless these results were in total agreement with the earlier findings of Kesselmeier *et al.* (1999) for the same arable soil and can be regarded as correct.

Steinbacher *et al.* (2004) used dynamic chambers in the field in order to measure COS exchange fluxes between the soil and the atmosphere. But they only detected slight dependencies of the COS flux on soil temperature. Their maximum COS uptake occurred at around 8 – 9°C and a nearly continuous reduction of the COS uptake was observed as the temperature increased from 10°C to 14.5°C. In contrast, earlier measurements of forest soil samples by Lehmann and Conrad (1996) showed a broad COS uptake maximum in the range of 10 – 40°C, which may be the result of different species with different temperature optima. In this regard, the results of Lehmann and Conrad (1996) and Steinbacher *et al.* (2004) illustrate the variability of gas exchange among different types of soil. However, a

comparison appears uncertain, because of the different environmental conditions, types of soil, treatment of soil samples, and especially because of the small heterogeneity identified in their studies. Nonetheless, this could give us a possible explanation for the behavior of the Surinam forest soil, which exhibited a maximum COS uptake in the broad range of 10 to 30°C at different WFPS, which was in contradiction with the findings for the four other soils. Bekku *et al.* (2003) measured soil respiration rate as an indicator of soil microbial activity and saw an exponentional increase with the increase of temperature in artic, temperate and tropical soils. However, the temperate soil became less sensitive to temperature when incubated at higher temperatures, in contrast to the artic and tropical soils which did not change in temperature dependence as the temperature increased.

4.3.3. Uptake of COS under varying soil water content (WC)

The exchange of trace gases is intimately related to the soil WC as the substrate supply for soil microorganisms is accomplished by diffusion of the substrates in the soil water films and as well because water in soil pores is the dominant controller of gaseous diffusion in soils (Meixner and Yang, 2006). The soil WC was therefore considered as the critical parameter for the uptake of COS (Conrad, 1996; Kesselmeier *et al.*, 1999).

In this study the COS uptake was continuously measured between the maximum soil WC (field capacity) and 0% WC of each soil type. The temperature was held constant during the experiments. Each soil exhibited a maximum V_d at another soil WC, although, at optimum temperatures the optimum soil WC for the German and Finnish soil were similar at 11.5% WC, this counted also for the Chinese and Siberian soil but at 9% WC. The deposition velocity for these two different soils was found to exhibit a maximum at the same optimum soil WC (9%) and WFPS (19%), and temperature range of 25 – 30°C, even when the pH differed in such a quantity.

4.3.3.a. WFPS parameter depends on soil WC, structure and number of pores

It is largely known that the parameter soil WC does not allow to evaluate and to compare trace gas exchange with soil. Instead, soil structure and pore number play a crucial role in gas diffusion. Therefore water-filled pore space (WFPS) was calculated according to the general particle density (ρ_S), considered to be 2.65 g/cm³ for most of the soils, and the bulk density

(ρ_b) (Hillel, 1980), which was separately determined for each soil (see 4.3.1.b). Surprisingly, the maximum V_d of the boreal soils (Chinese, Finnish and Siberian soil) coincided at the same WFPS optimum at around 19%, in contrast to the German soil which exhibited a maximum V_d at a significantly higher WFPS (near 29%). Figure 4.3 shows the deposition data of all four soils as the normalized relative V_d in percent (%), allowing a better estimate on how the comparable exchange pattern of four different soils around the world looked like.

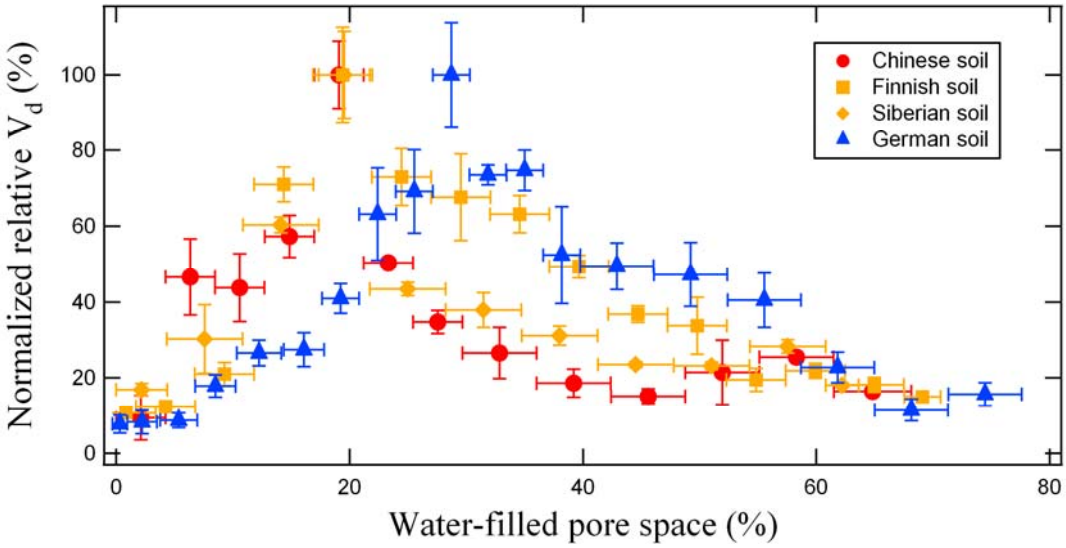

Figure 4.3: Normalized relative V_d (%) for the German, Chinese, Finnish and Siberian soil related to the WFPS at 15°C, 30°C, 25°C and 25°C, respectively. Optima for the boreal soils coincided around 19% WFPS, the German soil exhibited a maximum V_d at a higher WFPS. Each data point represents the mean value of at least 3 measurements with their standard errors.

Nevertheless, figure 4.3 gave convincing evidence that soil WC, soil structure and number of pores (bulk density) should be considered together when estimating the COS uptake by soils. To our knowledge, this was the first time that four totally different soils were compared and parameterized according to the WFPS and temperature.

Steinbacher *et al.* (2004) considered soil WC as an important parameter as well. They found low uptake rates under rather dry conditions and an increased uptake at around 1.6g H_2O per g dry weight. In addition they found a substantial uptake of COS at even much higher soil WCs. This completely contrasted with the laboratory measurements of Kesselmeier *et al.* (1999). They sampled over a range of soil WC from 0.05 to 0.42g H_2O per g dry weight (5 – 42%) and found a pronounced peak of COS uptake in the range of 10 – 15%, which declined

towards zero uptake at the lowest and highest soil WCs. However, this contrast could be explained by the following discrepancies: firstly there was an enormous difference in organic carbon content between the samples investigated in the laboratory study (1.4%) and the field studies (ranging from 47.3% at the top to 5.1% at 6cm depth); secondly the procedure of homogenizing soil samples for laboratory analysis could have an influence. It is well known that organic soils can act completely different compared to mineral soils. The five soils which were investigated in this study were all from mineral origin. Unfortunately, WFPS was never discussed in literature in relation to the uptake of COS by soils.

4.3.4. A 3-dimensional model for the V_d in relation to temperature and WFPS

Both, temperature and WFPS, seem to have a major role in the COS uptake by soils and should therefore be considered in the parameterization on a global scale (Figure 4.4). Three-dimensional plots of the fitted deposition velocities in relation to the observed temperatures and WFPS of the German, Chinese, Finnish and Siberian soil, respectively, demonstrate clearly the uptake behavior of the different soil types.

The V_d in the three-dimensional graphs were based on the mathematical best fits which were made according to the mathematical equation [7] introduced by Meixner and Yang (2006) (see section 2.4.2.). For that reason, maximum V_d in this graph were not directly based on the measured maximum V_d data points, but gave a good view on the importance of temperature and WFPS for the uptake of COS by different soils.

The German soil (Figure 4.4 A) exhibited a sharp peak-shaped optimum in the range of 15 to 17°C, a similar optimum temperature range was measured by Teusch (1998), which demonstrates the accuracy of the data and the reproducibility of measurements. The Chinese soil (Figure 4.4 B) exhibited a peak-shaped optimum in the range of 25 to 30°C and near 19% WFPS.

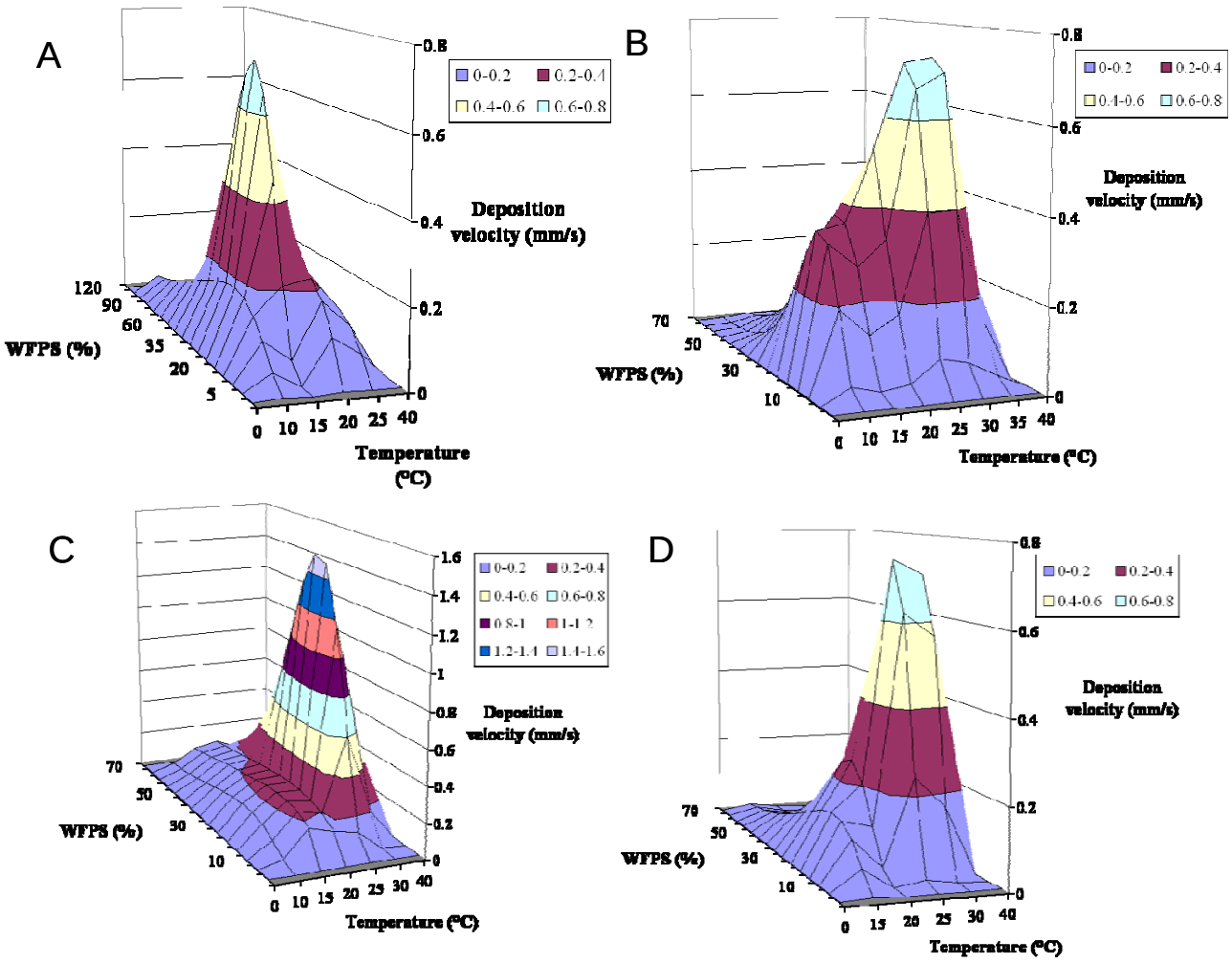

Figure 4.4: Modeling Deposition velocity (V_d; mm s^{-1}) of the German (A), Chinese (B), Finnish (C) and Siberian (D) soils in relation to temperature (°C) and WFPS (%). The mathematical equation [7] introduced by Meixner and Yang (2006) was used to fit the data. The V_d at 0°C and 40°C was virtually set to zero mm s^{-1}. Emission of COS was never observed under our natural set of experimental conditions.

In addition the Finnish arable soil (Figure 4.4 C) and the Siberian forest soil (Figure 4.4 D) exhibited a comparable exchange pattern as the Chinese arable soil at an optimum temperature between 25 and 30°C and a WFPS near 19%.

It is still inexplicable why soils from a more boreal climate show a rather high temperature optimum in the range between 25 and 30°C around a similar WFPS of 19%. In contrast, the German soil, which originates from a more temperate climate, performed an optimum around a lower temperature (15°C) and a higher WFPS (near 29%).

Remarkably, the Finnish soil exhibited a much higher maximum V_d in the range between 25 and 30°C and at the same WFPS near 19%. As discussed in section 4.3.1.b, a lower bulk density and thus a higher porosity could have a huge influence on the V_d maximum. This again illustrates the important role of diffusivity in the uptake of COS by soils.

Furthermore, the amplitude of the peak-shaped optimum is also influenced by the applied atmospheric mixing ratio (Teusch, 1998; Kesselmeier *et al.*, 1999).

4.4. The role of enzymatic activity

4.4.1. Literature motivation

The distinct role of temperature and WFPS in COS uptake presented in the optimum curves for the German, Chinese, Finnish and Siberian soil implied the involvement of a physiological or an enzymatic catalyzed process. Any cleavage of COS by chemical reactions can be excluded by the rather neutral and even acidic pH for the Siberian soil. Instead, an explanation for the typical uptake pattern of COS can be derived from the knowledge of the physiological background of the COS consumption in general.

Protoschill-Krebs *et al.* (1995, 1996), Blezinger *et al.* (2000) and Kuhn and Kesselmeier (2000) revealed that the key enzyme for the uptake of COS in higher plants, algae and lichens has been shown to be the carbonic anhydrase (CA) enzyme. Protoschill-Krebs *et al.* (1996) estimated the Michaelis-Menten constant (K_M), representing the affinity of an enzyme towards its substrate, in the case of isolated CA from pea plants. Since the K_M of CA for COS is 1000 fold smaller than the value of the K_M of CA for CO_2, CA has a higher affinity towards COS. Based on the higher affinity of CA towards COS they concluded that CA *in vivo* splits COS into CO_2 and H_2S and may feed the carboxylating enzymes ribulose-1,5-bis-phosphate carboxylase (Rubisco) and phosphoenolpyruvate carboxylase (PEP-Co).

The release of H_2S from cleavage of COS was investigated with the green algae *Chlamydomonas reinhardtii* by Protoschill-Krebs *et al*. (1995). The release of H_2S showed a close correlation to the consumption of COS, but a substantial part of the expected H_2S was missing. Nevertheless, this was most probably caused by application of a technique which involved a loss of 30 to 40% of the H_2S (Protoschill-Krebs *et al.*, 1995; Notni *et al.*, 2007).

Furthermore, Kesselmeier *et al.* (1999) indicated that CA could also play an important role in the uptake of COS by soils. They compared the uptake of COS of the soil sample with and without inhibition of the specific enzyme CA (Figure 1.10). The inhibition was carried out by the inhibitor 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ), which is a lipophylic inhibitor and CA activity should be inhibited both externally (i.e. at transport level) and internally (i.e. carboxysomal CA) (Palmquist *et al.*, 1994; Jaiswal *et al.*, 2005). The addition of EZ to the

soil sample resulted in a highly significant ($p < 0.001$) reduction of the COS uptake of more than 50%, showing CA to be one of the dominant factors for the consumption of COS by the investigated soil (Kesselmeier *et al.*, 1999). The extent of inhibition can differ from genera and is reflected by differences in their inherent potential and genetic background (Jaiswal *et al.*, 2005). CA is an ancient enzyme widespread in the Archaea and Bacteria domains and is recognized as an important enzyme for the photosynthesis in cyanobacteria (Badger and Price, 2003).

4.4.2. CA-activity in the five investigated soils

CA-activity was investigated for all five soils using a modified method of Wilbur and Anderson (1948). All soils were treated in the same way and seemed to show a distinct activity, though CA-activity data was still very scattered for each soil. Therefore, the results presented in this study are very preliminary. An overview on the CA-activity data is presented in Figure 4.5.

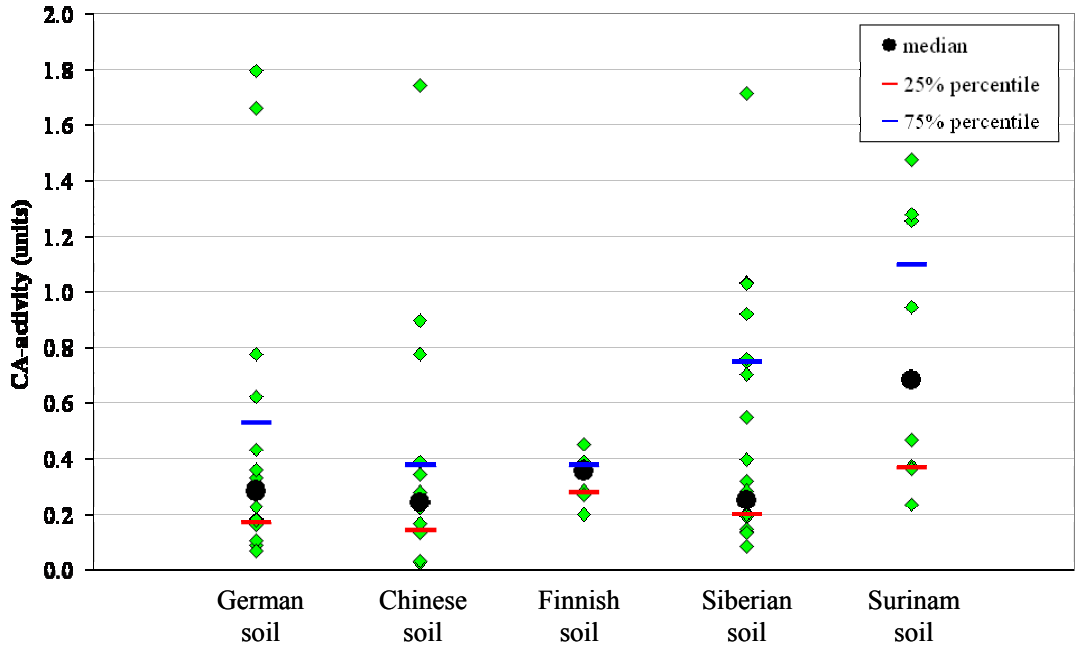

Figure 4.5: An overview of the CA-activity (units pro 400 mg soil, see 3.7) for each soil investigated. The green dots represent the data, the black dot the median, the line below the median represents the 25% percentile and the line above the median represents the 75% percentile.

Since this data is very preliminary and should be interpreted with caution, we based ourselves on the median which should give a better idea about the CA-activity of each soil instead of the average value. The median of the CA-activity of the five soils ranges between 0.24 and 0.68 units pro 400 mg soil. Unfortunately, to our knowledge there is no data available about CA-activity in soils to be compared with. Sandoval-Soto (2002) measured the CA-activity of the trees *Fagus sylvatica* L. and *Quercus ilex* L. and got an average of 5.23 ± 0.064 units per 2g plant material for the first tree and 16.75 ± 0.326 per 2g plant material for the latter. The amount of soil used in this study was only 400mg compared to 2g of plant material in the study of Sandoval-Soto (2002). If enzymatic activity is supposed to increase linear with the amount of soil or plant material used, the enzymatic activity of the soil samples should be multiplied by five in order to compare the activities of both samples.

Although this enzymatic activity data is assumed to be very preliminary, the results demonstrate that all soils investigated show enzymatic activity of CA. Together with the inhibition data of Kesselmeier *et al.* (1999) it clearly illustrates the importance of enzymatic activity in the uptake of COS by soils. Recent models (Schenk *et al.*, 2004; Yonemura *et al.*, 2005; Notni *et al.*, 2007) also confirm CA as one of the key enzyme for the uptake of COS. Thus, the physiologically based consumption of COS is assumed to be of major importance under natural conditions. But the physical parameter WFPS may be regarded as the dominant feature to understand COS exchange being strongly dependant on gas diffusion.

4.5. Conclusion

This study showed that it is undisputable that soil acts as a sink for COS. In addition the study confirmed the findings of Kesselmeier *et al.* (1999) for the German arable soil, which gave us a well funded motivation to investigate several soils around the world. In order to parameterize the uptake of COS by soils it was necessary to figure out the most important physical and biological factors which characterize the exchange between soils and the atmosphere. Three arable and two forest soils were examined and differed in soil structure, composition and pH.

Primarily, deposition velocities (V_ds) in relation to temperature and soil water content (WC) were considered. The optimum curve in the dependence of COS uptake on temperature could be explained by an enzymatically catalyzed process. An enzyme increases the turnover with increasing temperature, but this trend is superimposed by a decrease in activity if the temperature reaches a certain value owing to reorganization and/or denaturation of the enzyme structures (Kesselmeier *et al.*, 1999; Geng and Mu, 2004) and contributes less to the uptake. The exchange of trace gases is intimately related to the soil WC as the substrate supply for soil microorganisms is accomplished by diffusion of the substrates and water in soil pores is the dominant controller of gaseous diffusion in soils. Laboratory experiments in this study gave convincing data which emphasize an optimum-like behavior in relation to temperature as well to soil WC.

On the other hand and secondly, the optimum curves also underlined a possible biological factor. An explanation for the typical uptake pattern of COS can be derived from the knowledge of the physiological background of the COS consumption in general (Protoschill-Krebs *et al.*, 1995; Protoschill-Krebs *et al.*, 1996; Kesselmeier *et al.*, 1999; Kuhn and Kesselmeier, 2000). Carbonic anhydrase (CA) turned out to be the key enzyme for the uptake of COS by plants, algae, lichens and soils. Together with the inhibition data of Kesselmeier *et al.* (1999), the detected enzymatic activity of CA in all investigated soils, clearly illustrates the importance of enzymatic activity in the uptake of COS by soils. Recent models (Schenk *et al.*, 2004; Yonemura *et al.*, 2005; Notni *et al.*, 2007) also confirm CA as one of the key enzymes for the uptake of COS.

It is ubiquitous known that the field capacity is different for each soil type and is depending on the soil structure and number of pores. Therefore, WFPS was calculated and turned out to be an excellent parameter to describe the uptake of COS in relation to soil WC, soil structure and number of pores. The distinct influence of temperature and WFPS clearly demonstrated the importance of the physical characteristics of the soil, which indicates the major role of diffusivity in the exchange of gases between soils and the atmosphere. The linearity between bulk density (as indicator of porosity) and deposition velocity (figure 4.3) clearly demonstrate that even at optimum conditions for the enzymatic activity of CA (at optimum temperature and optimum WFPS) the quantity of COS uptake can differ according to the porosity or the size of the pores. In this regard, even when the enzymatic activity of CA can occur under optimal natural conditions (temperature and WFPS), diffusivity will remain the limiting factor. This study should allow a more realistic approach on the COS uptake by soils on a global scale.

5. Summary

Carbonyl sulfide (COS) is one of the most abundant and stable reduced sulfur trace gases found in the atmosphere with an ambient concentration around 500 ppt, which is involved in stratospheric aerosol production and the ozone cycle. COS has a variety of natural and anthropogenic sources but is well balanced by sinks as vegetation and soils. Since the sink strength of soils is poorly understood, it is important to characterize the controlling parameters. All of the soil exchange measurements done before 1990 presumed soils as a substantial source of COS (Castro and Galloway, 1991). In addition to the vegetation, soils are now regarded as an important sink (Watts, 2000).

Soil samples were investigated for their exchange of COS with the atmosphere under controlled ambient conditions. Three arable soils from Germany, China and Finland and 2 forest soils from Siberia and Surinam are parameterized in relation to the ambient COS concentration, temperature and soil water content (WC). Beside ambient concentration and soil WC, soil structure and enzymatic activity seem to control the direction as well as the magnitude of the flux between soils and the atmosphere. The matching optima for boreal soils in relation to water-filled pore space (WFPS) and the linearity between deposition velocity (V_d) and bulk density suggest that the uptake of COS depends on the diffusivity dominated by WFPS, a parameter depending on soil WC, soil structure and porosity of the soil. Since carbonic anhydrase (CA) has been identified as the controlling enzyme for COS uptake in soil, we qualitatively identified the activity of CA in our soil samples, but these results are considered to be very preliminary.

6. References

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7. Annex

7.1. Abbreviations

A	Soil surface
ABA	Abscisic acid
C	Carbon
C_{total}	Total carbon
Ca	calcium
CA	Carbonic anhydrase
CH_3SH	Methyl mercaptane
CO_2	Carbon dioxide
COS	Carbonyl sulfide
CS_2	Carbon disulfide
c_{ref}	Concentration of COS in reference cuvette
c_{sample}	Concentration of COS in sample cuvette
$C_6H_{13}NO_4$	Bicine
DMDS	Dimethyl disulfide
DMS	Dimethyl sulfide
D_0	Gas diffusion coefficient in free air
D_P	Gas diffusion coefficient
dw	Dry weight
Δc	Measured concentration difference
E	East
EDTA	Ethylene-diamine-tetraacetic acid
EZ	6-ethoxy-2-benzothiazole-2-sulfonamide or ethoxyzolamide
ε	Air-filled porosity
F	Gas exchange rate; pmol g^{-1} h^{-1}
f	amount of pores
Fa.	Company
FAO	Food and Agriculture Organization
FEP	Teflon
FPD	Flame Photometric Detector

GIS	Geographic Information System
H	Hydrogen
H^+	Hydrogen ion
ha	hectare
HCO_3^-	Bicarbonate
H_2O	Water
H_2S	Hydrogen sulfide
H_2SO_4	Hydrogen sulfate
hυ	Wavelength
ID	Inner diameter
ISRIC	International Soil Reference and Information Center
K	Potassium
K_{cat}	catalytic constant
K_M	Michaelis-Menten constant
kg m^{-2}	Kilogram per square meter
km	Kilometer
ln	Natural logarithms
Mg	Magnesium
mM	milli molair
mm s^{-1}	Millimeter per second
µm	Micrometer
µM	Micro molair
MPCh	Max Planck Institute for Chemistry
MPI	Max Planck Institute
N	Nitrogen
N_{total}	Total nitrogen
N	North
NaCl	Sodiumchloride
NaOH	Sodium hydroxide
nm	Nanometer
NPP	Net Primary Production
O	Oxygen
OH	OH-radical
P	Phosphorus

p	Probability
Pep-Co	Phosphoenol pyruvate-carboxylase
pH	Logarithms of H^+ concentration
PMSF	8-Phenylmethylsulphonylfluoride
ppm	10^{-6}, parts per million
ppt	10^{-12}, parts per trillion
PTFE	Polytetrafluorethylene
PVP	Poly-1-vinyl-2-pyrrolidon
Q	Chamber flush rate
RUBISCO	Ribulose-1,5-biphosphate-carboxylase
ρ_b	Bulk density
ρ_S	General particle density
Φ	Soil total porosity
S	Sulfur
S_{total}	Total sulfur
SO_2	Sulfur dioxide
SO_4^{2-}	Sulfate
$\sigma/\sqrt{n}$	Standard error
σ_{rel}	Relative precision
Tg a^{-1}	Terra gram per year
UK	United Kingdom
USA	United States of America
USDA	United States Department of Agriculture
V_d	Deposition velocity
W	West
WC	Water content
WFPS	Water-filled pore space
WLR	Water-reduced linear reduction

7.2. Data details

In this section data of each graph concerning COS uptake or deposition velocity (V_d) in relation to soil WC and WFPS is presented.

Table 7.1: German soil: measured COS uptake data (at 200g soil; pmol g^{-1} h^{-1}) and its standard error, temperature (°C), soil WC (%) and WFPS (%) which are presented in figure 3.1.

Temperature [°C]	Soil WC [%]	WFPS [%]	COS uptake at 200g [pmol g^{-1} h^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
15	49.50	124.94	3.230	1.486
	47.00	118.63	2.236	1.853
	44.50	112.32	5.094	4.692
	42.00	106.01	3.141	1.320
	39.50	99.70	8.402	1.401
	37.00	93.39	7.790	0.714
	34.50	87.08	5.799	1.333
	32.00	80.77	4.637	1.544
	29.50	74.46	8.193	1.111
	27.00	68.15	5.477	1.275
	24.50	61.84	9.948	1.990
	22.00	55.53	10.198	1.683
	19.50	49.22	15.035	1.607
	17.00	42.91	15.997	1.535
	14.50	36.60	18.927	1.552
	12.63	31.87	22.315	0.599
	11.38	28.71	25.004	2.071
	10.13	25.56	21.984	2.038
	8.88	22.40	17.666	2.157
	7.63	19.25	15.612	1.238
	6.38	16.09	10.449	1.512
	4.85	12.23	10.973	1.261
	3.38	8.52	8.390	1.181
	2.13	5.36	3.611	0.952
	0.88	2.21	4.659	1.170
	0.13	0.32	1.344	1.676
20	49.50	124.94	2.382	0.306
	47.00	118.63	2.071	0.209
	44.50	112.32	1.863	0.213
	42.00	106.01	1.791	0.411

	39.50	99.70	2.758	0.296
	37.00	93.39	3.460	0.323
	34.50	87.08	4.100	0.284
	32.00	80.77	4.362	0.264
	29.50	74.46	4.749	0.387
	27.00	68.15	4.023	0.696
	24.50	61.84	6.554	0.436
	22.00	55.53	7.539	0.362
	19.50	49.22	7.838	0.372
	17.00	42.91	7.666	0.216
	14.50	36.60	9.249	0.175
	12.63	31.87	9.076	0.269
	11.38	28.71	10.026	0.380
	10.13	25.56	9.740	0.216
	8.88	22.40	9.279	0.268
	7.63	19.25	9.186	0.092
	6.38	16.09	8.506	0.309
	4.85	12.23	6.751	0.163
	3.38	8.52	5.925	0.067
	2.13	5.36	5.869	0.300
	0.88	2.21	4.982	0.289
	0.13	0.32	3.404	0.171
25	49.50	124.94	0.836	0.340
	47.00	118.63	0.723	0.303
	44.50	112.32	1.133	0.187
	42.00	106.01	1.315	0.321
	39.50	99.70	1.742	0.438
	37.00	93.39	1.042	0.154
	34.50	87.08	1.696	0.163
	32.00	80.77	1.829	0.129
	29.50	74.46	0.990	0.271
	27.00	68.15	0.661	1.125
	24.50	61.84	1.533	0.177
	22.00	55.53	2.649	0.317
	19.50	49.22	4.261	0.680
	17.00	42.91	1.236	0.151
	14.50	36.60	1.536	0.077
	12.63	31.87	1.878	0.142
	11.38	28.71	6.046	0.0041
	10.13	25.56	6.158	0.103
	8.88	22.40	5.957	0.192
	7.63	19.25	6.297	0.182
	6.38	16.09	5.492	0.333
	4.85	12.23	4.749	0.325
	3.38	8.52	4.028	0.065

	2.13	5.36	3.367	0.251
	0.88	2.21	2.103	0.078
	0.13	0.32	1.705	0.253

Table 7.2: German soil: measured deposition velocity data (V_d at 80g; mm s^{-1}) and its standard error, temperature, soil WC (%) and WFPS (%) which are presented in figure 3.2, figure 3.3 and partially also in figure 3.7, figure 3.8, figure 3.12, figure 3.16, figure 3.20 and figure 3.21.

Temperature [°C]	Soil WC [%]	WFPS [%]	V_d at 80g [mm s^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
15	49.50	124.94	0.064	0.016
	47.00	118.63	0.050	0.024
	44.50	112.32	0.090	0.018
	42.00	106.01	0.059	0.018
	39.50	99.70	0.171	0.026
	37.00	93.39	0.188	0.021
	34.50	87.08	0.109	0.022
	32.00	80.77	0.095	0.026
	29.50	74.46	0.133	0.023
	27.00	68.15	0.097	0.020
	24.50	61.84	0.192	0.030
	22.00	55.53	0.342	0.101
	19.50	49.22	0.399	0.094
	17.00	42.91	0.417	0.069
	15.13	38.18	0.442	0.144
	13.88	35.02	0.630	0.079
	12.63	31.87	0.621	0.042
	11.38	28.71	0.844	0.248
	10.13	25.56	0.584	0.141
	8.88	22.40	0.533	0.142
	7.63	19.25	0.345	0.035
	6.38	16.09	0.231	0.034
	4.85	12.23	0.224	0.025
	3.38	8.52	0.150	0.021
	2.13	5.36	0.074	0.011
	0.88	2.21	0.071	0.020
	0.13	0.32	0.067	0.013
20	49.50	124.94	0.053	0.017
	47.00	118.63	0.046	0.011
	44.50	112.32	0.040	0.013
	42.00	106.01	0.040	0.024
	39.50	99.70	0.062	0.017

	37.00	93.39	0.077	0.019
	34.50	87.08	0.089	0.015
	32.00	80.77	0.100	0.018
	29.50	74.46	0.107	0.020
	27.00	68.15	0.094	0.041
	24.50	61.84	0.155	0.028
	22.00	55.53	0.183	0.022
	19.50	49.22	0.194	0.020
	17.00	42.91	0.201	0.016
	15.13	38.18	0.242	0.016
	13.88	35.02	0.247	0.009
	12.63	31.87	0.246	0.020
	11.38	28.71	0.273	0.024
	10.13	25.56	0.264	0.018
	8.88	22.40	0.256	0.019
	7.63	19.25	0.250	0.008
	6.38	16.09	0.231	0.023
	4.85	12.23	0.167	0.013
	3.38	8.52	0.137	0.013
	2.13	5.36	0.118	0.011
	0.88	2.21	0.086	0.038
	0.13	0.32	0.090	0.003
25	49.50	124.94	0.019	0.019
	47.00	118.63	0.016	0.017
	44.50	112.32	0.027	0.012
	42.00	106.01	0.032	0.020
	39.50	99.70	0.045	0.030
	37.00	93.39	0.022	0.009
	34.50	87.08	0.038	0.009
	32.00	80.77	0.040	0.007
	29.50	74.46	0.021	0.015
	27.00	68.15	0.016	0.046
	24.50	61.84	0.026	0.008
	22.00	55.53	0.049	0.019
	19.50	49.22	0.092	0.039
	17.00	42.91	0.094	0.010
	14.50	36.60	0.112	0.005
	12.63	31.87	0.126	0.008
	11.38	28.71	0.156	0.004
	10.13	25.56	0.159	0.006
	8.88	22.40	0.153	0.013
	7.63	19.25	0.163	0.014
	6.38	16.09	0.137	0.018
	4.85	12.23	0.111	0.020
	3.38	8.52	0.091	0.005

	2.13	5.36	0.074	0.016
	0.88	2.21	0.042	0.004
	0.13	0.32	0.025	0.002

Table 7.3: Chinese soil: measured deposition velocity data (V_d at 80g; mm s^{-1}) and its standard error, temperature, soil WC (%) and WFPS (%) which are presented in figure 3.5, figure 3.6 and partially also in figure 3.7, figure 3.8, figure 3.12, figure 3.20 and figure 3.21.

Temperature [°C]	Soil WC [%]	WFPS [%]	V_d at 80g [mm s^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
10	32.69	69.30	0.019	0.036
	30.69	65.06	0.102	0.027
	28.69	60.82	0.062	0.016
	26.69	56.58	0.031	0.025
	24.69	52.34	0.051	0.025
	22.69	48.10	0.045	0.011
	20.69	43.86	0.081	0.027
	18.69	36.62	0.157	0.015
	16.69	35.38	0.063	0.036
	14.69	31.14	0.217	0.032
	12.69	26.9	0.179	0.031
	10.69	22.66	0.293	0.042
	8.69	18.42	0.487	0.016
	8.00	16.96	0.334	0.025
	6.69	14.18	0.223	0.014
	4.69	9.94	0.150	0.035
	2.69	5.70	0.102	0.020
	0.69	1.46	0.123	0.031
15	32.69	69.30	0.080	0.017
	30.69	65.06	0.103	0.040
	28.69	60.82	0.106	0.010
	26.69	56.58	0.128	0.021
	24.69	52.34	0.137	0.038
	22.69	48.10	0.229	0.038
	20.69	43.86	0.175	0.023
	18.69	39.62	0.244	0.015
	16.69	35.38	0.168	0.018
	14.69	31.14	0.227	0.005
	12.69	26.90	0.52	0.037
	10.69	22.66	0.344	0.034
	9.5	20.14	0.422	0.029
	8.69	18.42	0.323	0.031
	6.69	14.18	0.245	0.027

	4.69	9.94	0.115	0.024
	2.69	5.70	0.147	0.025
	0.69	1.46	0.054	0.028
20	32.69	69.30	-0.080	0.022
	30.69	65.06	0.047	0.006
	28.69	60.82	-0.001	0.027
	26.69	56.58	0.139	0.011
	24.69	52.34	0.137	0.039
	22.69	48.10	0.107	0.007
	20.69	43.86	0.113	0.036
	18.69	39.62	0.185	0.027
	16.69	35.38	0.318	0.007
	14.69	31.14	0.193	0.001
	12.69	26.90	0.280	0.039
	10.69	22.66	0.240	0.011
	9.19	19.48	0.525	0.051
	7.94	16.83	0.314	0.073
	6.69	14.18	0.181	0.038
	4.69	9.94	0.094	0.035
	2.69	5.70	-0.003	0.028
	0.69	1.46	-0.035	0.051
25	30.09	63.79	0.143	0.024
	27.50	58.30	0.263	0.027
	24.50	51.94	0.220	0.036
	21.50	45.58	0.261	0.060
	18.50	39.22	0.223	0.021
	15.50	32.86	0.216	0.030
	13.00	27.56	0.558	0.013
	11.00	23.32	0.541	0.020
	9.00	19.08	0.814	0.069
	7.00	14.84	0.727	0.023
	5.25	11.13	0.531	0.004
	3.75	7.95	0.310	0.013
	2.25	4.77	0.200	0.020
	0.75	1.59	0.138	0.014
30	30.57	64.81	0.152	0.009
	27.50	58.30	0.236	0.012
	24.50	51.94	0.199	0.079
	21.50	45.58	0.140	0.018
	18.50	39.22	0.173	0.034
	15.50	32.86	0.247	0.063
	13.00	27.56	0.322	0.028
	11.00	23.32	0.467	0.006
	9.00	19.08	0.927	0.083
	7.00	14.84	0.531	0.051

	5.00	10.60	0.406	0.083
	3.00	6.36	0.432	0.093
	1.00	2.12	0.088	0.055
35	29.69	62.94	0.114	0.013
	26.69	56.58	0.231	0.000
	23.69	50.22	0.196	0.012
	20.69	43.86	0.246	0.018
	17.69	37.50	0.268	0.027
	14.69	31.14	0.367	0.040
	10.69	22.66	0.451	0.047
	7.69	16.30	0.330	0.052
	4.69	9.94	0.078	0.022
	1.69	3.58	0.053	0.005

Table 7.4: Finnish soil: measured deposition velocity data (V_d at 80g; mm s^{-1}) and its standard error, temperature, soil WC (%) and WFPS (%) which are presented in figure 3.10, figure 3.11 and partially also in figure 3.7, figure 3.12, figure 3.20 and figure 3.21.

Temperature [°C]	Soil WC [%]	WFPS [%]	V_d at 80g [mm s^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
10	41.12	69.40	0.155	0.029
	38.50	64.98	0.178	0.028
	35.50	59.92	0.175	0.008
	32.50	54.85	0.168	0.015
	29.50	49.79	0.151	0.013
	26.50	44.73	0.169	0.016
	23.50	39.66	0.209	0.018
	20.50	34.60	0.217	0.011
	17.50	29.54	0.194	0.010
	15.00	25.32	0.257	0.011
	13.00	21.94	0.275	0.003
	11.00	18.57	0.287	0.010
	9.00	15.19	0.234	0.004
	7.00	11.81	0.192	0.016
	5.00	8.44	0.139	0.009
	3.00	5.06	0.118	0.005
	1.00	1.69	0.113	0.006
15	41.14	69.43	0.132	0.013
	38.50	64.98	0.132	0.023
	35.50	59.92	0.167	0.010
	32.50	54.85	0.146	0.012
	29.50	49.79	0.123	0.014
	26.50	44.73	0.180	0.013

	23.50	39.66	0.169	0.010
	20.50	34.60	0.194	0.012
	17.50	29.54	0.234	0.009
	14.50	24.47	0.244	0.011
	11.50	19.41	0.268	0.009
	8.50	14.35	0.283	0.019
	5.50	9.28	0.202	0.018
	2.50	4.22	0.121	0.010
	0.50	0.84	0.115	0.013
20	41.03	69.25	0.054	0.007
	38.50	64.98	0.045	0.010
	35.50	59.92	0.046	0.006
	32.50	54.85	0.060	0.010
	29.50	49.79	0.112	0.007
	26.50	44.73	0.095	0.012
	23.50	39.66	0.116	0.006
	20.50	34.60	0.085	0.005
	17.50	29.54	0.082	0.013
	14.50	24.47	0.166	0.012
	11.50	19.41	0.222	0.003
	8.50	14.35	0.125	0.015
	5.50	9.28	0.059	0.015
	2.50	4.22	-0.004	0.008
	0.50	0.84	-0.023	0.003
25	40.93	69.08	0.231	0.017
	38.50	64.98	0.281	0.030
	35.50	59.92	0.338	0.030
	32.50	54.85	0.301	0.046
	29.50	49.79	0.521	0.116
	26.50	44.73	0.567	0.034
	23.50	39.66	0.760	0.045
	20.50	34.60	0.973	0.076
	17.50	29.54	1.012	0.176
	14.50	24.47	1.125	0.116
	11.50	19.41	1.541	0.194
	8.50	14.35	1.095	0.070
	5.50	9.28	0.324	0.048
	2.50	4.22	0.191	0.012
	0.50	0.84	0.167	0.009
30	40.59	68.51	-0.027	0.012
	38.50	64.98	0.148	0.049
	35.50	59.92	0.118	0.061
	32.50	54.85	0.310	0.000
	29.50	49.79	0.272	0.065
	26.50	44.73	0.139	0.072

	23.50	39.66	0.211	0.031
	20.50	34.60	0.258	0.060
	17.50	29.54	0.585	0.014
	14.50	24.47	0.749	0.024
	11.50	19.41	0.799	0.055
	8.50	14.35	0.192	0.003
	5.50	9.28	0.220	0.020
	2.50	4.22	0.079	0.015
	0.50	0.84	-0.038	0.005

Table 7.5: Siberian soil: measured deposition velocity data (V_d at 80g; mm s^{-1}) and its standard error, temperature, soil WC (%) and WFPS (%) which are presented in figure 3.14, figure 3.15 and partially also in figure 3.16, figure 3.20 and figure 3.21.

Temperature [°C]	Soil WC [%]	WFPS [%]	V_d at 80g [mm s^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
15	27.93	60.66	0.088	0.004
	25.50	55.39	0.099	0.002
	22.50	48.87	0.090	0.004
	19.50	42.35	0.098	0.004
	16.50	35.84	0.132	0.007
	13.50	29.32	0.135	0.008
	11.00	23.89	0.137	0.003
	9.00	19.55	0.147	0.004
	6.50	14.12	0.132	0.005
	3.50	7.60	0.118	0.005
	1.00	2.17	0.112	0.013
20	27.87	60.53	0.093	0.009
	25.50	55.39	0.124	0.009
	22.50	48.87	0.098	0.004
	19.50	42.35	0.102	0.007
	16.50	35.84	0.135	0.008
	13.50	29.32	0.188	0.006
	11.00	23.89	0.323	0.050
	9.00	19.55	0.164	0.008
	6.50	14.12	0.105	0.011
	3.50	7.60	0.089	0.008
	1.00	2.17	0.088	0.008
25	28.65	62.23	0.157	0.005
	26.50	57.56	0.245	0.015
	23.50	51.04	0.201	0.009
	20.50	44.53	0.204	0.007
	17.50	38.01	0.269	0.021

	14.50	31.49	0.328	0.040
	11.50	24.98	0.376	0.015
	9.00	19.55	0.865	0.099
	6.50	14.12	0.522	0.018
	3.50	7.60	0.262	0.078
	1.00	2.17	0.146	0.014
30	27.60	59.95	0.045	0.003
	25.50	55.39	0.090	0.000
	22.50	48.87	0.113	0.006
	19.50	42.35	0.115	0.008
	16.50	35.84	0.138	0.011
	13.50	29.32	0.239	0.076
	11.00	23.89	0.469	0.031
	9.00	19.55	0.803	0.030
	6.50	14.12	0.256	0.018
	3.50	7.60	0.082	0.007
	1.00	2.17	0.099	0.020

Table 7.6: Surinam soil: measured deposition velocity data (V_d at 80g; mm s^{-1}) and its standard error, temperature, soil WC (%) and WFPS (%) which are presented in figure 3.18 and figure 3.19.

Temperature [°C]	Soil WC [%]	WFPS [%]	V_d at 80g [mm s^{-1}]	Standard Error ($\sigma/\sqrt{n}$)
10	41.25	58.45	0.115	0.060
	39.00	55.26	0.137	0.039
	37.00	52.43	0.059	0.010
	35.00	49.60	0.141	0.031
	33.00	46.76	0.060	0.042
	31.00	43.93	0.049	0.029
	29.00	41.09	0.074	0.031
	27.00	38.26	0.135	0.035
	25.00	35.43	0.068	0.027
	23.00	32.59	0.123	0.023
	21.00	29.76	0.098	0.015
	19.00	26.92	0.218	0.045
	17.00	24.09	0.245	0.043
	15.00	21.26	0.213	0.041
	7.00	9.92	0.321	0.031
	5.00	7.09	0.028	0.018
	3.00	4.25	0.036	0.032
	1.00	1.42	0.064	0.011
15	41.00	58.10	0.032	0.061

	38.00	53.85	0.127	0.038
	35.00	49.60	0.109	0.033
	32.00	45.35	0.135	0.051
	29.00	41.09	0.141	0.030
	26.00	36.84	0.071	0.014
	23.00	32.59	0.105	0.017
	20.00	28.34	0.295	0.033
	17.00	24.09	0.144	0.050
	14.00	19.84	0.035	0.017
	11.00	15.59	0.053	0.019
	8.00	11.34	0.031	0.022
	5.00	7.09	0.068	0.016
	2.00	2.83	0.077	0.043
20	41.00	58.10	0.115	0.005
	38.00	53.85	0.103	0.021
	35.00	49.60	0.068	0.042
	32.00	45.35	0.040	0.031
	29.00	41.09	0.139	0.058
	26.00	36.84	0.283	0.030
	23.00	32.59	0.143	0.038
	20.00	28.34	0.122	0.042
	17.00	24.09	0.049	0.014
	14.00	19.84	0.053	0.011
	11.00	15.59	0.063	0.019
	8.00	11.34	0.059	0.020
	5.00	7.09	0.060	0.022
	2.00	2.83	0.042	0.012
25	41.00	58.10	0.175	0.024
	38.00	53.85	0.085	0.019
	35.00	49.60	0.082	0.010
	32.00	45.35	0.291	0.033
	29.00	41.09	0.319	0.019
	26.00	36.84	0.126	0.028
	23.00	32.59	0.125	0.027
	20.00	28.34	0.047	0.010
	17.00	24.09	0.034	0.013
	14.00	19.84	0.069	0.015
	11.00	15.59	0.046	0.011
	8.00	11.34	0.071	0.017
	5.00	7.09	0.043	0.021
	2.00	2.83	0.108	0.017
30	41.00	58.10	0.159	0.046
	38.00	53.85	0.156	0.020
	35.00	49.60	0.114	0.004
	32.00	45.35	0.176	0.042

	29.00	41.09	0.132	0.016
	26.00	36.84	0.237	0.036
	23.00	32.59	0.132	0.012
	20.00	28.34	0.320	0.028
	17.00	24.09	0.311	0.032
	14.00	19.84	0.216	0.005
	11.00	15.59	0.227	0.011
	8.00	11.34	0.208	0.017
	5.00	7.09	0.151	0.028
	2.00	2.83	0.128	0.018

8. Curriculum vitae

Personal information

Name: Heidi Van Diest

E-mail:

Born: November 21st, 1980 in Diest, Belgium

Sex: Female

Nationality: Belgian

Marital Status: Not married

Education

1986 – 1992:

Primary school, Katholiek basisonderwijs Schaffen, Belgium.

1992 – 1998:

Secondary school, Athenaeum Prins van Oranje, Diest, Belgium.

1998 – 2003:

Master's degree (*cum laude*) in Biology at Catholic University Leuven, Belgium;
Thesis title: The Role of Polyamines in Apical Dominance in *Phaseolis vulgaris* L.;
Supervisor: Prof. Dr. Jan Geuns;

October 2003 – June 2007:

PhD in Biology at "Gutenberg Universität, Fachbereich Biologie" Mainz and Max Planck Institute for Chemistry Mainz, Germany;
Thesis title: Diffusivity and enzymatic activity control the exchange of Carbonyl Sulfide (COS) between soils and the atmosphere;
Supervisor: Prof. Dr. Jürgen Kesselmeier;

October 2003 – June 2007:

Student at the International Max Planck Research School (IMPRS) in Mainz, Germany.