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Observations of the uptake of carbonyl sulfide (COS) by trees under elevated atmospheric carbon dioxide concentrations

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Abstract. Global change forces ecosystems to adapt to elevated atmospheric concentrations of carbon dioxide (CO_2). We understand that carbonyl sulfide (COS), a trace gas which is involved in building up the stratospheric sulfate aerosol layer, is taken up by vegetation with the same triad of the enzymes which are metabolizing CO_2, i.e. ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco), phosphoenolpyruvate carboxylase (PEP-Co) and carbonic anhydrase (CA). Therefore, we discuss a physiological/biochemical acclimation of these enzymes affecting the sink strength of vegetation for COS. We investigated the acclimation of two European tree species, *Fagus sylvatica* and *Quercus ilex*, grown inside chambers under elevated CO_2, and determined the exchange characteristics and the content of CA after a 1–2 yr period of acclimation from 350 ppm to 800 ppm CO_2. We demonstrate that a compensation point, by definition, does not exist. Instead, we propose to discuss a point of uptake affinity (PUA). The results indicate that such a PUA, the CA activity and the deposition velocities may change and may cause a decrease of the COS uptake by plant ecosystems, at least as long as the enzyme acclimation to CO_2 is not surpassed by an increase of atmospheric COS. As a consequence, the atmospheric COS level may rise causing an increase of the radiative forcing in the troposphere. However, this increase is counterbalanced by the stronger input of this trace gas into the stratosphere causing a stronger energy reflection by the stratospheric sulfur aerosol into space (Brühl et al., 2012). These data are very preliminary but may trigger a discussion on COS uptake acclimation to foster measurements with modern analytical instruments.

1 Introduction

Aside from sulfur dioxide (SO_2), carbonyl sulfide (COS) is the most abundant sulfur gas in the atmosphere with relative constant mixing ratios of 450–500 ppt and a lifetime of more than two years (Khalil et al., 1984; Mihalopoulos et al., 1991; Bandy et al., 1992; Barnes et al., 1994; Kjellström, 1998; Montzka et al., 2007; Barkley et al., 2008). Due to this long lifetime, COS can be transported up into the stratosphere where it contributes to stratospheric ozone chemistry (Crutzen, 1976; Andreae and Crutzen, 1997). In times of low volcanic activity, COS may serve as a source of sulfur to the stratospheric aerosol layer by conversion to sulfuric acid (Junge et al., 1961; Crutzen, 1976), contributing to the backscattering of radiation energy into space. Thus, the stratospheric cooling effect by the COS derived sulfate particles can be regarded to approximately cancel the warming tendency as caused by the direct radiative forcing by the trace gas COS within the troposphere (Brühl et al., 2012).

The global budget of COS has been estimated as being balanced within the ranges of uncertainties (Watts, 2000; Kettle et al., 2002). However, this balance is a matter of debate both for the sources and the sinks, especially with regard to terrestrial vegetation which acts as the main sink for this trace gas and which is reported to be heavily underestimated (Notholt et al., 2003; Mu et al., 2004; Sandoval-Soto et al., 2005; Campbell et al., 2008; Suntharalingam et al., 2008; Van Diest and Kesselmeier, 2008). This is valid for the Northern Hemisphere, whereas the Southern Hemisphere seems to be strongly influenced by the oceans (Montzka et al., 2007).

The biological background for the uptake of COS by vegetation is understood to be the combined action of the carboxylation enzymes Ribulose-1,5-bisphosphate carboxylase-oxygenase (Rubisco; EC 4.1.1.39), Phosphoenolpyruvate Carboxylase (PEP-Co; EC 4.1.1.31) and the key enzyme carbonic anhydrase (CA; EC 4.2.1.1), which were previously reported to be involved in the exchange of carbon dioxide (CO_2) and carbonyl sulfide (COS) (Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1995, 1996; Schenk et al., 2004; Yonemura et al., 2005; Notni et al., 2007). This enzymatic model consisting of three enzymes assigns a key role for CA and has been confirmed very recently by Stimler et al. (2011). Furthermore, the close relationship between COS and CO_2 uptake enhances discussions to use COS as a tracer for canopy photosynthesis, transpiration and stomatal conductance (Wohlfahrt et al., 2012; Seibt et al., 2010). The role of CA has also been demonstrated in cases of lichens and soils (Kesselmeier et al., 1999; Kuhn and Kesselmeier, 2000; Van Diest and Kesselmeier, 2008), thus demonstrating the dominant role of this enzyme which is obviously also responsible for the toxicity of inhaled COS due to metabolization to hydrogen sulfide (Thiess et al., 1968; Chengelis and Neal, 1980). Of special interest within this context are recent findings about the identification of a CS_2 hydrolase acting similarly to carbonic anhydrase by splitting CS_2 into H_2S and CO_2 in a thermophilic Archeon obtaining energy from reduced sulfur compounds (Smeulders et al., 2011).

Changes in the enzyme's activities will have consequences for the exchange of CO_2 and COS between plants and the atmosphere. Elevated atmospheric CO_2 can cause an immediate increase of photosynthetic CO_2 uptake. However, on a long-term basis this initial stimulation of photosynthesis is often followed by a decline which is obviously caused by a decrease in activities of the carboxylating enzymes Rubisco, PEP-Co and CA. Acclimation of Rubisco is well established (Drake et al., 1997; Moore et al., 1999; Stitt and Krapp, 1999; Possell and Hewitt, 2009), though the mechanism of this kind of acclimation is a matter of debate (Rogers and Ellsworth, 2002). A decrease of Rubisco and PEP-Co activities would lead to a loss of COS uptake capacity by these enzymes. In contrast, fewer reports are available for CA, though an acclimation of the key enzyme CA might have even stronger impact. High CO_2 levels caused a decrease of CA activity in cucumber (Peet et al., 1986) and cotton (Chang, 1975). An increase of the CA mRNA steady state level was found in *Arabidopsis* (Cervigni et al., 1971), whereas enzyme activities and their transcript levels were reduced in pea plants grown under elevated CO_2 (Majeau and Coleman, 1996). These observations are in close accordance with Sage (2002), who reported about a potential reduction of the CA gene transcription. Also, the green alga *Chlamydomonas reinhardtii* adapts its CA activity to an increase in the environmental CO_2 level with a decrease in the enzyme activity (Spencer et al., 1983; Coleman et al., 1984; Protoschill-Krebs et al., 1995). Long-term observations, however, are not known to us. Besides enzymatic acclimation, a reduction of stomatal conductivity under long-term elevated CO_2 enrichment also contributes to the acclimation of photosynthesis (Herrick et al., 2004). Thus, the growth of plants under elevated CO_2 may cause an acclimation to the CO_2 availability by reducing the stomatal uptake as well as enzymatic activities. Reduction of stomatal apertures will seriously affect the deposition of COS which is taken up through the stomata (Sandoval-Soto et al., 2005). A decrease in the CA activities as a consequence of elevated CO_2 will affect the metabolic COS consumption by plants, as demonstrated earlier with the green alga *Chlamydomonas reinhardtii* which adapts to high CO_2 levels by decreasing its CA activity (Protoschill-Krebs et al., 1995).

In view of our knowledge as briefly reviewed above, we may postulate the hypothesis that elevated CO_2 in the long term will lead to a decrease of enzymatic activities and thus to a shift of potential compensation points, which reflect the ambient concentration at which the consumption balances production resulting in a net flux of zero (Kesselmeier and Merk, 1993; Conrad, 1994; Lehmann and Conrad, 1996; Simmons et al., 1999; Conrad and Meuser, 2000). Elevated CO_2 will trigger a decrease of the enzymatic activities, which is balanced by a higher CO_2 availability. Thus, the CO_2 uptake may not decline, but a CA acclimation may lead to a reduction of the COS uptake due to a lower metabolic sink as long as the uptake is not also enhanced by higher substrate (i.e. COS) concentration. Furthermore, increased CO_2 without an increase of COS may lead to a competitive inhibition of the COS consumption. Thus, changes in the COS uptake capacity should become visible in a shift of a potential compensation points. Therefore, we investigated the acclimation of two European tree species, *Fagus sylvatica* and *Quercus ilex*, grown inside chambers under elevated CO_2, and determined the exchange characteristics and the content of CA after a 1–2 yr period of acclimation from 350 ppm to 800 ppm CO_2.

2 Materials and methods

2.1 Plant material and growth

The tree species (3–4 yr old) investigated were holm oak (*Quercus ilex* L.) and European beech (*Fagus sylvatica* L.). From March 1998 to February 2000, the trees were grown in a greenhouse at 25° C under a 12/12 h light–dark regime with a light intensity of 600 µmol m^{-2} s^{-1} of photons (PAR) and a relative humidity of 70 %. CO_2 concentrations were adjusted using pure CO_2 from commercially available cylinders and held constant at 800 ppm CO_2 (±20 ppm) or at about 350 ppm (with some variation between 330 to 450 ppm). For details see Peuser et al. (1995) and Peuser and Wild (1996). Three individuals of each tree species were investigated.

2.2 Enclosure system (cuvettes) and gas exchange measurements

Measurements of COS exchange were time consuming and had to be spread over several days up to a few weeks. Table 1 gives an overview of the measurement schedule in order to note potential seasonal effects.

Gas exchange of enclosed tree branches (6–10 leaves) was investigated using a dynamic (flow-through) Teflon film cuvette system consisting of a plant measuring and an empty reference cuvette with 9 l of volume each. The Teflon FEP film (0.05 µm thickness) was obtained from Norton Saint-Gobain performance plastic (Germany). This cuvette system has been operated in previous studies (Schäfer et al., 1992; Kesselmeier et al., 1993, 1996; Kuhn et al., 2000; Sandoval-Soto et al., 2005). The system was designed for measurements of volatile organics and sulfur compound gas exchange in the laboratory as well as in the field, and to have minimal effects on such trace gases. All experiments were performed inside a climate chamber with identical conditions as compared to the growth chamber. Trace gas sampling was accompanied by measurements of ambient CO_2, CO_2 exchange and transpiration by an infra-red gas analyzer (LiCor 6262, LiCor Inc., Lincoln, Nebraska, USA). Transpiration rates and CO_2 exchange were calculated based on the concentration differences between the outlet ports of the branch cuvette and the empty cuvette (see below). Stomatal conductances were calculated according to von Caemmerer and Farquhar (1981) with cuvette air temperatures assigned as leaf temperatures.

COS and CO_2 mixing ratios were adjusted by mixing purified compressed air gas mixtures derived from a permeation device (Haunold, Germany) with COS permeation tubes (VICI Metronics, Santa Clara, California) and CO_2 from a pressurized bottle (Messer-Griesheim, Germany). For details see Sandoval-Soto et al. (2005). COS concentrations were adjusted between 230–1700 ppt (10–70 nmol m^{-3}).

COS was quantified by an automated in situ analysis of volatile sulfur gases by real time sampling at both cuvettes according to von Hobe et al. (2008). With a home built automated Sulfur Gas Analyser (SUGAR), sulfur compounds were cryogenically trapped, thermally desorbed and analyzed by gas-chromatographic separation and flame-photometric detection.

Gas exchange rates (F) were calculated according to Eq. (1)

$$F = \Delta c(Q/A) \quad (1)$$

considering the concentration differences between the sample and reference cuvette ($\Delta c = c_{\text{sample}} - c_{\text{ref}}$; [pmol m^{-3}]) and the chamber flush rate (Q; [m^{-3} s^{-1}]). All exchange rates were related to the enclosed leaf area (A; [m^2]). Leaf area was determined by a calibrated scanner system (ScanJET IICX with DeskSCAN II; both Hewlett-Packard, USA), and SIZE 1.10 (Müller, Germany). For details see Sandoval-Soto et al. (2005).

2.3 Determination of carbonic anhydrase activity

Carbonic anhydrase (CA) activity was determined in leaf homogenates (leaf extracts) by an electrometric technique according to Wilbur and Anderson (1948). This method measured the pH drop caused by the catalytically driven CO_2 dissociation at 0 °C. The CA activity was given in dimensionless units according to Porter and Grodzinski (1983) comparing the speed of the pH decrease with and without the enzyme (leaf extract).

2.4 Statistical analysis

The linear relationship between substrate availability and the uptake rates was assessed statistically by the analysis of the Pearson's correlation coefficient relating the COS concentration in the reference cuvette to the exchange rate. Further information was obtained regarding the R^2 of the regression analysis of the linear model

$$\boldsymbol{F} = \beta_0 + \beta_1 \boldsymbol{c_R} + \boldsymbol{\varepsilon} \quad \text{(Model 1)} \quad (2)$$

with $\boldsymbol{F}$ and $\boldsymbol{c_R}$ indicating the exchange rate (dependent variable) and reference cuvette concentration of COS (independent variable), respectively. β_0 and β_1 reflect the regression coefficients and ε the residuals.

For further analysis, the linear model was extended by introducing the CO_2 concentration under which the trees were growing during the experiment ($\boldsymbol{CO_2}$) accompanied by the interaction between $\boldsymbol{c_R}$ and $\boldsymbol{CO_2}$ ($\boldsymbol{c_R} * \boldsymbol{CO_2}$) leading to the more complex model:

$$\boldsymbol{F} = \beta_0 + \beta_1 \boldsymbol{c_R} + \beta_2 \boldsymbol{CO_2} + \beta_3 (\boldsymbol{c_R} * \boldsymbol{CO_2}) + \boldsymbol{\varepsilon} \quad \text{(Model 2)} \quad (3)$$

with β_2 and β_3 again reflecting the corresponding regression coefficients. Again, R^2 provides information about the quality of the model. Furthermore, p-values indicate the significance for the exchange triggers $\boldsymbol{CO_2}$ and $\boldsymbol{c_R} * \boldsymbol{CO_2}$. Here, the values of type III sum of squares (SS) are taken into account. If the influence of $\boldsymbol{CO_2}$ is significant, both groups within one data set (one tree) are different. Significance concerning the interaction indicates that both groups within the analyzed data set are significantly different if projected to the y-axis ($\boldsymbol{F}$). Finally, interaction may also indicate differences of the linear slope.

Besides these analyses regarding the linear relationship of exchange rate and COS concentration, several mean value comparisons were performed by the two-sided Student's t-test. The null hypothesis that no difference exists between the two means μ_1 and μ_2 was tested against the alternative with an existing difference, i.e.,

$$H_0 : \mu_1 = \mu_2 \text{ versus } H_1 : \mu_1 \neq \mu_2. \quad (4)$$

Again, corresponding p-values indicate the significance of the results. A p-value less than 5 % indicates a significant difference.

Table 1. Schedule of measurements of trees grown constantly under the indicated CO_2 regimes beginning in March 1998. Three individuals of each tree species in each growth regime were consecutively measured.

	CO_2 regime (ppm)	Measurement window
Fagus sylvatica	350	27 August–15 September 1998
	800	15 September–23 September 1998
	350	5 July–13 July 1999
	800	8 June–28 June 1999
	350	8 October–1 November 1999
	800	13 September–7 October 1999
Quercus ilex	350	8 June–20 August 1998
	800	21 July–4 August 1998
	350	29 April–5 May 1999
	800	19 May–1 July 1999
	350	17 December–26 December 1999
	800	7 February–17 February 2000

The group comparisons were carried out with each tree and for each measuring period comparing the influence of the two CO_2 concentrations. Thus, means of leaf conductance, CA and the deposition velocities of COS and CO_2 were compared.

All above mentioned statistical analyses were performed with SAS, Version 9.1.

The differences of the point of uptake affinity (PUA), a new term to understand the correlation between COS concentration and uptake in the absence of a compensation point, were checked by the 95 % confidence intervals of the linear model 1 for $F = 0$ (Sigma Plot 11).

3 Results

3.1 Leaf conductances, deposition velocities and CA activities

Elevated CO_2 was expected to affect several physiological parameters reflecting gas exchange under acclimation conditions. Table 2 gives an overview of leaf conductances (COND; $\mathrm{mmol\,m^{-2}\,s^{-1}}$), CO_2 and COS deposition velocities (V_d; $\mathrm{mm\,s^{-1}}$; quotient exchange rate/concentration and from linear model 1, respectively), as well as carbonic anhydrase activities of trees grown under the indicated CO_2 regimes as observed in the course of the three years experiment. European beech grown under 800 ppm CO_2 exhibited significantly reduced leaf conductances (H_2O) in August/September 1998 and September/October 1999 and significantly increased conductances in June/July 1999. Holm oak exhibited significantly lower conductances for the June–August 1998 data only. CO_2 deposition velocities (V_{dCO_2}) exhibited a more consistent behavior. In all cases we found significantly lower V_{dCO_2} under elevated CO_2 with p-values < 0.001.

Due to the variable COS concentrations, the deposition velocities for COS (Table 2) were derived from the slope of the regression line plotting the exchange data against the reference gas phase COS concentration. Generally, the V_{dCOS} was lower under elevated CO_2. However, these differences were not significant with p-values > 0.05 in the case of all beech data, and in the case of holm oak for the April/July 1999 data. Furthermore, it has to be noted that a general acclimation trend, i.e. a development of V_{dCOS} with incubation length, was not observed for beech, whereas a steady increase in the case of holm oak under elevated CO_2 might exist.

As elucidated in the introduction, the uptake of COS is based on the consumption by the enzymatic triad Rubisco, PEP-Co, and carbonic anhydrase (CA), with CA regarded as the key enzyme. Table 2 gives an overview of the amount of CA activity measured within the leaves of the tree individuals growing under elevated CO_2. A decrease of the CA activity under elevated CO_2 was found in the case of holm oak in April/July 1999 and December 1999/February 2000, although these differences were not significant.

3.2 Correlation between COS uptake and environmental COS concentrations

A clear increase of COS uptake was observed in relation to increasing ambient COS concentration with all trees and during all measurement times. Thus, in plotting a regression line a point of intersection with the x-axis could be expected. However, with the exception of a few single points (Fig. 1, *Fagus sylvatica* Sep/Oct 1999) we never observed an emission of COS. In view of this result, we will not discuss a compensation point but regard the estimated intersection with the x-axis as an indicator of substrate affinity in relation to the enzymatic background. We call it point of uptake affinity (PUA). Table 2 gives an overview of the ranges of PUA as derived from the regression studies; given are the intersections

Table 2. Leaf conductances (COND; mmol m^{-2} s^{-1}), CO_2 deposition velocities (V_{dCO_2}; mm s^{-1}; quotient exchange rate/concentration), COS deposition velocities (V_{dCOS}; mm s^{-1}; from slope of linear model 1), carbonic anhydrase activities (non-dimensional units according to Wilbur and Anderson, 1948) and point of uptake affinities (PUA) of trees grown under the indicated CO_2 regimes. Incubation under the indicated CO_2 concentration started in March 1998. Significance of difference mean values between 350 and 800 ppm growth regimes are indicated by p-values according to a two-sided Student's t-test (SAS Version 9.1). p-values > 0.05 indicate non-significant differences and nd = no data. PUAs were calculated according to model 1. The ranges for the 95 % confidence intervals were obtained from the intersections of the confidence bands with the x-axis (c_R) (Sigma Plot 11).

	CO_2 regime ppm	COND ± SD mmol m^{-2} s^{-1}	p-values	V_{dCO_2} ±SD mm s^{-1}	*N* COND V_{dCO_2}	p-values	V_{dCOS} ± SD (slope) mm s^{-1}	*N*	p-values	CA activity ±SD	*N*	p-values	COS PUA ppt	95 % Conf. Interval ppt
Fagus sylvatica														
August/September 1998	350	69.1 ± 8.7	<0.001	0.24 ± 0.023	177	<0.001	0.922 ± 0.123	46	0.109	4.90 ± 0.96	9	0.968	255	188–305
	800	42.6 ± 5.1		0.07 ± 0.006	135		0.646 ± 0.146	45		4.88 ± 0.96	7		207	0–317
June/July 1999	350	45.8 ± 9.2	<0.001	0.34 ± 0.061	312	<0.001	1.454 ± 0.163	68	0.229	5.32 ± 1.07	9	0.311	220	122–287
	800	72.3 ± 24.1		0.17 ± 0.025	146		1.253 ± 0.141	82		5.80 ± 0.86	9		227	104–316
September/October 1999	350	29.0 ± 9.3	<0.001	0.25 ± 0.027	672	<0.001	0.883 ± 0.058	141	0.126	nd			202	183–226
	800	21.3 ± 4.6		0.07 ± 0.009	213		0.787 ± 0.094	71		nd			282	157–377
Quercus ilex														
June/August 1998	350	58.7 ± 10.3	<0.001	0.25 ± 0.038	288	<0.001	0.967 ± 0.100	62	0.008	17.8 ± 5.2	9	0.589	224	166–272
	800	47.8 ± 4.6		0.12 ± 0.008	198		0.761 ± 0.081	66		16.5 ± 4.8	9		204	137–258
April/July 1999	350	43.2 ± 5.2	0.246	0.38 ± 0.041	338	<0.001	0.929 ± 0.084	67	0.963	18.6 ± 7.7	10	0.087	179	119–173
	800	42.0 ± 9.8		0.18 ± 0.025	228		0.926 ± 0.087	76		11.8 ± 7.3	7		330	251–397
December 1999 / February 2000	350	35.5 ± 6.0	0.08	0.29 ± 0.046	885	<0.001	1.538 ± 0.101	194	0.002	18.9 ± 2.4	9	0.109	184	173–193
	800	36.8 ± 4.2		0.15 ± 0.014	567		1.271 ± 0.097	189		16.9 ± 2.6	9		269	232–300

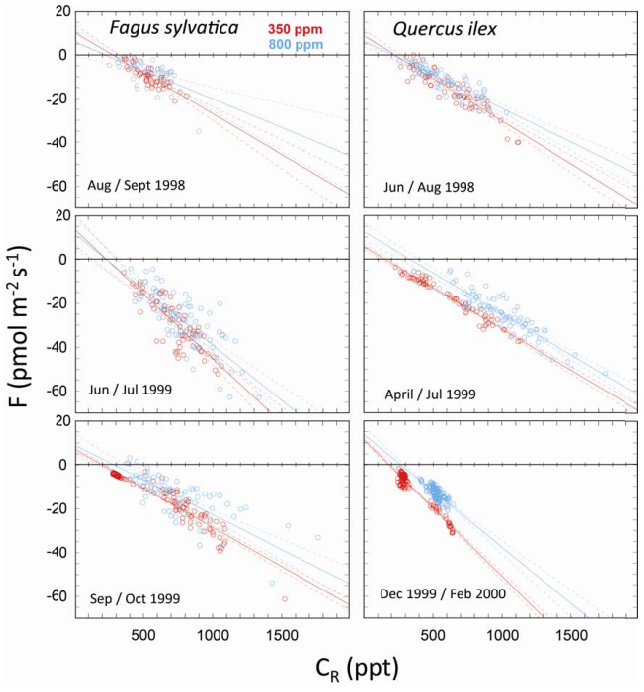

Fig. 1. Linear regression analysis of the relation between the initial COS concentration (c_R) and the uptake by European beech (*Fagus sylvatica*) and holm oak (*Quercus ilex*) growing under two different CO_2 regimes (350 and 800 ppm) beginning in March 1998 and measured at the indicated time periods. Given are the regression lines (continuous lines) together with their 95 % confidence bands (broken lines).

of the regression line with the x-axis plus the ranges of the 95 % confidence level. We observed a shift of the PUA towards higher values during continuous growth of the trees under elevated CO_2. In the case of holm oak (*Quercus ilex*), this shift is clearly demonstrated for two consecutive measurement periods 1999 and 1999/2000 (Fig. 1; Table 2). European beech (*Fagus sylvatica*) showed a similar trend related to the growing conditions within the measurement period September/October 1999; however, the confidence intervals still overlap, indicating non-significance. Unfortunately, no data could be reported for a second year for this species due to limited growth and measurement capacities.

3.3 Statistical significance of the differences between flux data sets

Table 3 presents an overview on the correlation and regression analyses performed. As indicated by a Pearson's correlation coefficient (P_c) < -0.7 (Table 3), except for the data set with beech in 1998 (800 ppm CO_2), we observed a strong linear relationship between the exchange flux (F) and the initial COS concentration as determined within the empty reference cuvette (c_R). Even for the exception, *Fagus sylvatica* at 800 ppm with a P_c of -0.58, we also detected a correlation. This result demonstrates that the linear model 1 is able to describe the variances well.

Adding the long-term growth regimes (CO_2 concentration), as described by linear model 2 (Table 3), drastically changes R^2. As expected, the new values lie between those separated according to their growth regime (see Table 3). The best description was found in the case of holm oak for the year 1999 ($R^2 = 0.91$) followed by holm oak in the year 2000 ($R^2 = 0.88$). For all other data sets, the variances are within the range of 51 to 83 %. Regarding the type III SS values, only in the case of holm oak (1999) could a highly significant difference between the 350 and 800 ppm regimes be found ($p<0.001$). In the case of all other measurement sets, such an acclimation could not be statistically proved, though sometimes a trend may be discussed. However, often both data clouds overlap at the start of the incubation, and in the case of beech during the whole observation time (Fig. 1). All together we may summarize that a statistically sound difference between the exchange behaviors of trees growing under elevated as compared to normal CO_2 was only found for the holm oak after one year of acclimation. In this special case the linear slope is nearly identical indicating very similar deposition velocities, whereas the two other oak data sets exhibit significantly different slopes. For beech trees identical slopes cannot be excluded because of the large p-values.

3.4 Global impact

Deposition velocities (V_d) are key for calculating fluxes and for estimating COS uptake versus CO_2 uptake rates to derive GPP related global sink estimates. We recalculated the global sink strength of vegetation based on our previous estimation (Sandoval-Soto et al., 2005) taking only those ecosystems into consideration with the two tree species as major contributors. Furthermore, we assume that the GPP is not altered because of physiological acclimation (decrease of enzymatic activities and stomatal aperture). With this approach, we estimate a decrease in the COS sink strength due to changed deposition velocities and enzymatic activities from 0.367–0.687 to 0.337–0.542 Tg a^{-1}, representing a decrease of 8–21 %.

4 Discussion

4.1 Leaf conductances, deposition velocities and CA activities

Acclimation to elevated CO_2 is reported to result in a reduction of the stomatal opening as a main factor (Paoletti and Gellini, 1993; Ceulemans and Mousseau, 1994; Ainsworth and Long, 2005). However, the data as presented in our study were biased by seasonal development because of the labor-intensive and time consuming measurements which were spread over several weeks for each period. Thus, not all of the data compared exhibited a significant reduction of stomatal

Table 3. Correlation (Pearson's coefficient, P_c) and regression analysis (R^2; see Fig. 1) according to model 1 regarding the correlation between the initial COS concentration in the reference cuvette (c_R) and the exchange flux (SAS Version 9.1). Regression analysis (R^2; see Fig. 1) according to model 2 regarding the correlation between the initial COS concentration in the reference cuvette (c_R) and the exchange flux. Model 2 describes the results taking into account the growth regime (SAS Version 9.1).

Plant species Year	Growth regime CO_2 (ppm)	Model 1		Model 2		
		P_c	R^2	R^2	Type III SS–CO_2	Type III SS–$CO_2 * c_R$
					p-values	
Fagus sylvatica (Sep 1998)	350	−0.858	0.736	0.511	0.280	0.109
	800	−0.585	0.342			
Fagus sylvatica (June/July 1999)	350	−0.842	0.709	0.654	0.775	0.229
	800	−0.783	0.614			
Fagus sylvatica (Sept/October 1999)	350	−0.954	0.910	0.799	0.362	0.126
	800	−0.786	0.619			
Quercus ilex (June/August 1998)	350	−0.917	0.840	0.831	0.208	0.008
	800	−0.878	0.770			
Quercus ilex (May/July1999)	350	−0.981	0.962	0.907	<0.001	0.963
	800	−0.917	0.841			
Quercus ilex (Dec 1999/Jan2000)	350	−0.968	0.938	0.884	0.182	0.002
	800	−0.763	0.582			

aperture caused by elevated CO_2 (Table 2). We consider the non-significance for the evergreen species holm oak within the "winter measurements" to be a seasonal effect. Similarly, the missing significance for the April/July data may be related to different physiological activities of the oak species in the course of this pair of measurements. Contrasting the expectations, the beech data for summer 1999 showed a significant increase of stomatal conductance under elevated CO_2. This increase may be understood to be caused by plant development between the June and July measurements. In July we noted a higher transpiration with all three tree individuals investigated in this case (data not shown). Nevertheless, excluding the June/July 1999 measurements for beech, the leaf conductance data indicated a decreasing trend over time in relation to the growth regime. This behavior is in close accordance with Herrick et al. (2004), who reported a decrease of stomatal conductance for sweetgum leaves under CO_2 enrichment. Contrasting the conductance data, a significant decrease of the CO_2 deposition velocities under elevated CO_2 was observed in all cases.

The COS deposition velocities were lower under elevated CO_2 in nearly all cases. However, these differences were not significant. Interestingly, with the exception of beech in June/July and September/October 1999, a steady increase of V_{dCOS} was found under 800 ppm CO_2. Such a development of V_{dCOS} is in accordance with data observed with sweetgum (White et al., 2010) but contrasts with the behavior of loblolly pine trees as reported by the same authors. However, we should have in mind that the third measurement period for the oak species was scheduled for a winter period, which limits a consistent interpretation.

We regard the decrease of V_{dCOS} under elevated CO_2 as a consequence of a competitive inhibition of the enzymes responsible for COS/CO_2 uptake by the higher number of CO_2 molecules competing for the same binding site. On a first view this seems to be contrasting Stimler et al. (2010b), who reported missing cross-inhibition effects between COS and CO_2. We agree that increasing COS does not inhibit CO_2 uptake, which seems to be reasonable comparing ppm with ppt. However, the effect of high CO_2 on the metabolism of COS does not really support their view. Regarding Fig. 6 in Stimler et al. (2010b), we got the impression that the increasing CO_2 in all assays led to a slight decrease of the COS uptake beginning at 450 ppm CO_2. Stimler et al. (2010b) themselves state that at high CO_2 concentration, the uptake of CO_2 continued to increase whereas the uptake of COS became saturated. The authors relate this behavior to synchronization with stomatal conductance and conclude that there is no inhibitory effect of CO_2 on COS uptake. The related data sets are not convincing as there is a decrease of COS uptake, and we think that a competitive inhibition cannot be excluded. We came to similar conclusions investigating the uptake of COS by decaying leaf litter (no active stomata) with decreasing uptake of COS under high respiration rates (Kesselmeier and Hubert, 2002). Furthermore, studies modeling the consumption of COS by carbonic anhydrase (Schenk et al., 2004; Notni et al., 2007) demonstrate the similarity of the enzymatic handling of COS as compared to CO_2. If we have to assume that CO_2 and COS compete for the same binding site, we cannot exclude

competitive inhibition, especially as we measured under an 800 ppm growth regime.

The determination of the CA enzymatic activities under current and elevated CO_2 did not show a clear result. Whereas beech did not show any acclimation, the holm oak data may be discussed indicating a long-term acclimation with a decrease of CA activity under elevated CO_2, which fits into the overall picture that acclimation of CA can be expected (Sage, 2002). Furthermore, the difference between European beech and holm oak is striking. The oak exhibits a three times higher amount of CA.

4.2 Correlation between COS uptake and environmental COS concentrations

We found a clear correlation of the COS uptake with ambient COS concentrations. Thus, an intersection of the regression line with the x-axis would reflect a so-called compensation point, which is defined as the result of the balance of consumption and production with a net exchange of zero (Conrad, 1994). Hence, an increase of the COS compensation point may be understood as a decrease of metabolic consumption, caused by a decrease of the enzyme affinity towards the substrate or a decrease of the enzymatic activity itself. As we observed a potential for decrease in the case of *Quercus ilex* (see above), an analysis of the flux data became highly interesting. Although not significant, CA activity after growth under high CO_2 levels tends to be lower than under normal levels (Table 2), though this acclimation seemed to decrease in the second year. However, we did not observe any emission of COS under our experimental conditions with 350 ppm CO_2, and only a few data points under elevated CO_2. Hence, as production of COS is missing, we are referring in this paper to a "virtual" compensation point, i.e. the intersection point of the extrapolated regression line of linear model 1 with the x-axis (Fig. 1). We propose to call this a point of uptake affinity (PUA), reflecting substrate affinity and enzyme activity. It can be noted that the PUA changes under elevated CO_2 (Table 2). For holm oak the data provide evidence that it adapts to elevated CO_2 levels by shifting the PUA, indicating a decrease of the COS uptake capacity induced by high CO_2 levels under long-term conditions. Beech, however, exhibits only a trend but supports a similar interpretation.

4.3 Global impact

Based on the few tree species investigated under elevated CO_2 so far, this approach has to be regarded as very preliminary. However, it contributes to the discussion of how elevated CO_2 might affect the global COS budget and balance (White et al., 2010). The increase of CO_2 levels, impacting the enzymatic adjustment (CA, Rubisco, PEP-Co) of plants, may cause a decrease of COS uptake as indicated by the V_{dCOS} based estimates and the potential shift of PUA. As a consequence, the atmospheric COS level may rise and cause an increase of the direct radiative forcing by this trace gas. However, this potential contribution to global warming is counterbalanced by the cooling effect of the COS derived stratospheric sulfate aerosol (Brühl et al., 2012). Our estimates of a decrease of the COS sink strength of vegetation, correcting the Sandoval-Soto et al. (2005) database, range between 8–21 %. This estimate is highly dependent on the potential increase of anthropogenic sources. Such an increase is discussed based on reports by Montzka et al. (2004) and Aydin et al. (2008) indicating that present COS levels of 500 ppt are greatly increased over preindustrial levels with a drastic increase of 200 ppt in 19th and 20th centuries. With regard to such a steep increase which resembles that of the CO_2 record, the potential decrease by the acclimation of the metabolic background of COS uptake could be expected to be balanced by a higher uptake rates due to higher substrate availability.

5 Conclusions

Growth of two European tree species under elevated CO_2 for nearly two years resulted in changes of the exchange patterns for CO_2 and COS, which in case of *Quercus ilex* supports the hypothesis that elevated CO_2 may lead to a reduction of the COS uptake capacity. Beech exhibited a significant decrease in leaf conductance under elevated CO_2, accompanied by small and insignificant decreases of V_{dCOS}. In contrast, holm oak exhibited no significant decrease of leaf conductance for 1999 and the winter values as well, but nevertheless a significant decrease of V_{dCOS} in June/August 1998 and December 1999/February 2000. Within this picture, it seems to be of interest that holm oak was found to have a 3–4 times higher CA activity and appears to be more sensitive to elevated CO_2. Furthermore, in the case of holm oak a significant shift of COS point of uptake affinity (PUA) was found. Such a shift may be regarded as a result of a complex mixture of driving forces, such as substrate availability depending on changes in gas concentrations and leaf conductances, and the influence of enzymatic activities depending on the amount of the active enzyme and its substrate affinity. Under elevated CO_2 we expect a decrease of enzyme activity of CA. Also, changes caused by competitive inhibition (increasing CO_2) can be expected. The results support the hypothesis that an acclimation of plants to a higher CO_2 level by decreasing their enzymatic capacity for CO_2 exchange will decrease the COS uptake, though an anthropogenic COS increase might neutralize this effect. Nevertheless, a visible decrease of the metabolic capacity for consuming COS should be detectable in form of an increase of the PUA. The data presented in our study support this hypothesis, though the database of two tree species is limited, our study was too short, and it was biased by plant development due to the time consuming measurements. Furthermore, it is an open question as to how

far this change in COS uptake is caused only by a decrease in CA activity, or also by adaptation of other enzymes such as PEP-Co and Rubisco. Answers to these questions may be found by continuous field investigations within Free Atmospheric Carbon Enrichment (FACE) sites, which offer advantages such as more natural conditions as compared to growth chamber incubation. FACE sites are suitable for more continuous and simultaneous measurements to investigate the relationships between exchange fluxes, atmospheric concentration and incubation history, and plant exchange regulations and metabolic capacities. Furthermore, modern online analytic techniques for COS determination (Stimler et al., 2010a, 2011) will add insight into these exchange processes in real time and avoid biases by seasonal development.

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