**Biogeosciences Discussions**

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

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## Abstract

Global change affects 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 enzmyes which are metabolizing the $CO_2$, i.e. Ribulose-1,5-bisphosphate Carboxylase-Oxygenase (Rubisco), Phosphoenolpyruvate Carboxylase (PEP-Co) and carbonic anhydrase (CA). Therefore, we discuss a physiological/biochemical adaptation of these enzymes to affect the sink strength of vegetation for COS. We investigated the adaption 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 adaption from 350 ppm to 800 ppm $CO_2$. We could demonstrate that the COS compensation point, the CA activity and the deposition velocities may change and cause a decrease of the COS uptake by plant ecosystems. As a consequence, the atmospheric COS level may rise leading to higher input of this trace gas into the stratosphere and causing a higher energy reflection by the stratospheric sulfur aerosol into space, thus counteracting the direct radiative forcing by the tropospheric COS.

## 1 Introduction

Aside from sulfur dioxide ($SO_2$) carbonyl sulfide (COS) is the most abundant sulfur gas in the atmosphere with relative constant concentrations 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 supplier 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 troposhere (Brühl et al., 2012).

5 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.,
10 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
15 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
20 enzymatic model 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 discussion to use COS as a tracer for canopy photosynthesis, transpiration and stomatal conductance (Wohlfahrt et al., 2011; Seibt et al., 2010). The role of CA has also been demonstrated in case of lichens and soils (Kesselmeier et al., 1999;
25 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

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$CS_2$ 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 initialize an immediate increase of photosynthetic $CO_2$ uptake. But on a long term basis this initial stimulation is often followed by a decline of photosynthesis which is obviously caused by a decrease of enzyme activities. Acclimation of Rubisco is well reported (Drake et al., 1997; Moore et al., 1999; Stitt and Krapp, 1999; Possell and Hewitt, 2009), however the mechanism of this kind of adaptation 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 related to these enzymes. In contrast, only a few reports are available for CA, though an adaptation of the key enzyme CA might have even stronger impact. High $CO_2$ levels caused an increase of the CA mRNA steady state level 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). 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). Overall, the acclimation of CA is not well documented but it can be predicted (Sage, 2002). 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 adaptation 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).

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In view of our knowledge as briefly reviewed above, we may postulate the hypothesis that elevated $CO_2$ on the long term will lead to a decrease of enzymatic activities and thus to a shift of compensation points, which reflect the ambient concentration at which the consumption balances production resulting in a net flux of zero (Kesselmeier and Merk, 1993; 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 will 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 (COS) concentration. Furthermore, increased $CO_2$ without an increase of COS leads to a competitive inhibition of the COS consumption. Thus, changes of the COS uptake capacity should become visible in a shift of the compensation point. Therefore, we investigated the adaption 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 adaption 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).

## 2.2 Enclosure system (cuvettes) and exchange measurements

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

Gas exchange of enclosed tree branches was investigated using a dynamic (flow-through) Teflon-film-cuvette system consisting of a plant measuring and an empty reference cuvette. 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. 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 was quantified in the ppt range by an automated analytical system according to Von Hobe et al. (2008) by consecutive sampling at both cuvettes. The exchange rates ($F$) were calculated according to the equation:

$$F = \Delta c \cdot (Q/A)$$

considering the concentration differences between the sample and reference cuvette ($\Delta c = c_{sample} - c_{ref}$) and the chamber flush rate ($Q$). All exchange rates were related to the enclosed leaf area ($A$). 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).

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## 2.3 Statistical analysis

The linear relationship between substrate availability and the uptake rates was assessed statistically by the analysis of the Pearson 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:

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

with $F$ and $c_R$ indicating the exchange rate (dependent variable) and reference cuvette concentration of COS (independent variable), respectively. $\beta_0$ and $\beta_1$ reflect the regression coefficients and $\varepsilon$ 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 ($CO_2$) accompanied by the interaction between $c_R$ and $CO_2$ ($c_R * CO_2$) leading to the more complex model:

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

with $\beta_2$ and $\beta_3$ 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 triggers $CO_2$ and $c_R * CO_2$. Here the values of type III Sum of Squares (SS) are taken into account. If the influence of $CO_2$ 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 ($F$). Finally, interaction may also be indicated in 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 $\mu_1$ and $\mu_2$ was tested against the alternative with an existing difference, i.e.:

$$H_0 : \mu_1 = \mu_2 \quad \text{vs.} \quad H_1 : \mu_1 \neq \mu_2.$$

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

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 compensation points were checked by the 95 % confidence intervals of the linear model 1 for $F = 0$ (Sigma Plot 11).

# 3 Results and discussion

## 3.1 Leaf conductances and deposition velocities

The data as presented in this study can be discussed on a measurement period related basis and on a long term trend. The latter is, however, a very limited approach as the measurement schedule is biased by seasonal effects because of the labor-intensive and time consuming measurements spread over several weeks for each period. Tables 2–4 give an overview about the development of leaf conductances and deposition velocities of $CO_2$ and COS as observed in the course of the three year experiment. As expected, for measurements with beech in August 1998 and October 1999 and during the first series for the oak species (June–August 1998) leaf conductances (Table 2) for water vapor were found to be significantly different for plants grown under 350 vs. 800 ppm $CO_2$ as elevated $CO_2$ triggers a reduction of stomatal aperture. This observation is in close accordance with earlier interpretations suggesting a reduction in the stomatal opening as a main factor (Paoletti and Gellini, 1993; Ceulemans and Mousseau, 1994; Ainsworth and Long, 2005). 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 can be related to different physiological activities of the oak species in the course of this pair of measurements.

The beech data for summer 1999 showing a significantly higher conductance under elevated $CO_2$ are not understood, but might be biased by plant development related to the earlier measurements in June as compared to the July measurements under 350 ppm $CO_2$. We noted a higher transpiration with all three tree individuals investi-
5    gated in this case (data not shown). Excluding the June/July 1999 measurements with 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.

10    $CO_2$ deposition velocities ($V_{dCO_2}$) exhibited a more consistent behavior (Table 3). In all cases we found a much lower $V_{dCO_2}$ for the measurements under elevated $CO_2$. All differences were highly significant with p-values $< 0.001$. Contrasting the conductance data, a constant development related to elevated $CO_2$ by adaptation of old leaves or by modified new leaves could not be observed. However, a clear increase was found
15    for beech growing at 800 ppm comparing the measurement period August/September 1998 with June/July 1999, which is in accordance with data for sweetgum as reported by White et al. (2010).

Contrasting the calculation of deposition velocities for $CO_2$ from the quotients of single measurement points (because of missing $CO_2$ variation) those for COS (Table 4)
20    could be derived from the slope of the regression line from the plot of the exchange data against the reference gas phase COS concentration data. The results show that in general the $V_{dCOS}$ is lower under elevated $CO_2$. However, these differences are not significant with p-values $> 0.05$ in the case of all beech data and for the spring data in the case of holm oak. A general adaptation trend, i.e. a development of $V_{dCOS}$ with incu-
25    bation length was not observed for beech, whereas there might be a steady increase in the case of holm oak under elevated $CO_2$. This development 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, in our case, the third measurement period for the oak species was scheduled for a winter period, which limits a

consistent interpretation. For the comparisons within each period we regard the decrease of $V_{dCOS}$ under elevated $CO_2$ as a consequence of competitive inhibition of the responsible enzymes for COS/$CO_2$ uptake by the higher number of $CO_2$ molecules.

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 being the key enzyme. Table 5 gives an overview about the amount of CA activity measured within the leaves of the tree individuals growing under elevated $CO_2$. Differences in the CA activity were found in the case of holm oak in April/May 1999 and December 1999/January 2000, although these differences were not significant. However, this seems to indicate that long term adaptation may lead to 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.

## 3.2 Compensation point for COS

An increase of the COS compensation points may be understood as a decrease of metabolic consumption, depending on substrate availability and enzymatic activities. Hence, an increasing compensation point may be understood as a decrease of carbonic anhydrase (CA) activity. 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 5) though this adaptation seemed to decrease in the second year. It has to be stated here that 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, 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). Based on this analysis, we observed a shift of COS compensation points 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

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for two consecutive measurement periods 1999 and 1999/2000 (Fig. 1; Table 6). European beech (*Fagus sylvatica*) showed a similar trend 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. Nevertheless, it can be noted that the compensation point for beech growing under 350 ppm $CO_2$ decreases whereas it increases under elevated $CO_2$. Table 6 gives an overview of the ranges of compensation points as derived from the regression studies; given are the intersections of the regression line with the x-axis plus the ranges of the 95 % confidence level. The data provide evidence that holm oak adapts to elevated $CO_2$ levels by shifting compensation points 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.

### 3.3 Statistical significance of the differences between flux data sets

Tables 7–8 present an overview on the correlation and regression analyses performed. As indicated (Table 7) by a Pearson Correlation Coefficient ($P_c$) < −0.7 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 8) $R^2$ drastically changes. As expected, the new values lie between those separated according to their growth regime (see Table 7). 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 to 800 ppm regime be

found ($p < 0.001$). In the case of all other measurement sets such an adaptation 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 adaptation. 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 according to Sandoval-Soto et al. (2005). With this approach the flux of COS is related to the uptake of $CO_2$ as described by the following equation:

$$F_{COS} = F_{CO_2} \cdot (V_{dCOS}/V_{dCO_2}) \cdot (M_{COS}/M_{CO_2})$$

$F_{COS}$  Flux of COS
$F_{CO_2}$  Flux of $CO_2$, NPP or GPP in $Tg\,a^{-1}$
$V_{dCOS}$  Deposition velocity of COS in $mm\,s^{-1}$
$V_{dCO_2}$  Deposition velocity of $CO_2$ in $mm\,s^{-1}$
$M_{COS}$  Molar mass of COS in ambient air
  (600 ppt equivalent to $1451\,ng\,m^{-3}$ at 25° and 1 atm)
$M_{CO_2}$  Molar mass of $CO_2$ in ambient air
  (350 or 800 ppm equivalent to 620 or $1419\,mg\,m^{-3}$ at 25° and 1 atm).

Thus, the COS/$CO_2$ $V_d$ ratios as derived from our measurements allow the assessment of the effect of elevated $CO_2$ on vegetation acting as a sink for COS. We performed an

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analysis in close accordance with our previous work (Sandoval-Soto et al., 2005) taking into account the $V_d$ values as given in Tables 3 and 4. Table 9 summarizes the result. As these data were derived from the slope of the linear model 1 (linear regression) the new $V_{dCOS}$ data are integrating over the whole range of COS concentrations, contrasting the older calculation based on single data (Flux/concentration) ratios. These new COS deposition velocities were found to range a little higher causing a higher COS/$CO_2 V_d$ ratio. Consequently, the COS sink strength for those ecosystems with trees as measured in the present study (*Quercus ilex* and *Fagus sylvatica*) rises from 0.397 to 0.688 Tg (maximum) and would cause a total increase from 1.404 to 1.696 Tg a$^{-1}$ (maximum) based on NPP, both values to be doubled for GPP. For discussion of the effect of elevated $CO_2$ we take only those ecosystems into consideration with the two tree species as major contributors, i.e. temperate evergreen and temperate deciduous forests, woodland and scrubland, savannah and desert and semi desert scrub. Furthermore, we assume that the GPP is not altered because of physiological adaption (decrease of enzymatic activities and stomatal aperture). With this approach, we estimate a decrease in the COS sink strength from 0.367–0.687 to 0.337–0.542 Tg a$^{-1}$, representing a decrease of 8–21 %. Based on the few tree species investigated under elevated $CO_2$ so far this approach has to be regarded as very preliminary. But it stresses how elevated $CO_2$ might affect the global COS budget and balance. 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 $V_d$ based estimates and the potential shift of compensation points. As a consequence, the atmospheric COS level may rise and cause an increase of the direct radiative forcing by this trace gas, which is however counterbalanced by the cooling effect of the COS derived stratospheric sulfate aerosol (Brühl et al., 2012).

## 4   Conclusions

Growth of two European tree species under elevated $CO_2$ for nearly two years resulted in some significant changes of the exchange patterns for $CO_2$ and COS which support the hypothesis that elevated $CO_2$ may lead to a reduction of the COS uptake capacity. Beech for example exhibits a significant decrease in leaf conductance under elevated $CO_2$, accompanied by a significant decrease of $V_{dCOS}$ for summers 1998 and 1999. In contrast, holm oak exhibits no significant decrease of leaf conductance for 1999 and the winter values as well, but nevertheless a significant decrease of $V_{dCOS}$ in all cases. 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 against adaption under elevated $CO_2$. Furthermore, in the case of holm oak, a significant shift of the COS compensation point was found. Such a shift may be regarded as a result of a complex mixture of triggers such as substrate availability depending on changes of gas concentrations and leaf conductances, and the influence of enzymatic activities depending on the amount of the enzyme and its availability for the corresponding metabolic step. In the case of the triad CA, Rubisco and PEP-Co, not only a decrease of enzyme activity, but also changes caused by competitive inhibition (increasing $CO_2$) can be expected. The results support the hypothesis that an adaptation of plants to a higher $CO_2$ level by decreasing their enzymatic capacity for the $CO_2$ exchange will affect the COS uptake. Consequently, a visible decrease of the metabolic capacity for consuming COS could be related to an increase of the compensation point. The data presented in our study support this hypothesis though the data base with two tree species is limited, our study was too short, and was biased by plant development due to the time consuming measurements. Furthermore, it is an open question whether this change in COS uptake is caused only by a decrease of CA activity, or also by adaptation of other enzymes such as PEP-carboxylase and Rubisco. Answers to these questions may be found for example by continuous field investigations within Free Atmospheric Carbon Enrichment (FACE) sites, which offer advantages such as more natural conditions as compared

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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 as well as plant physiological background to determine exchange regulations and metabolic capacities. Furthermore, modern online analysis techniques for COS determination (Stimler et al., 2010, 2011) will be able to add insight into these exchange processes in real time.

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**Table 1.** Schedule of measurements of trees grown constantly under the indicated $CO_2$ regimes beginning 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 |

**Table 2.** Leaf conductance (COND; $mmol\,m^{-2}\,s^{-1}$) of trees grown under the indicated $CO_2$ regimes ($n = 100$–200). Incubation under the indicated $CO_2$ concentration started in March 1998. Significance of differences of the COND mean values between 350 and 800 ppm growth regimes is 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.

| | $CO_2$ regime ppm | Mean COND $mmol\,m^{-2}\,s^{-1}$ | SD | p-values |
|---|---|---|---|---|
| *Fagus sylvatica* | | | | |
| Aug/Sep 1998 | 350 | 69.1 | 8.7 | <0.001 |
| | 800 | 42.6 | 5.1 | |
| Jun/Jul 1999 | 350 | 45.8 | 9.2 | <0.001 |
| | 800 | 72.3 | 24.1 | |
| Sep/Oct 1999 | 350 | 29.0 | 9.3 | <0.001 |
| | 800 | 21.3 | 4.6 | |
| *Quercus ilex* | | | | |
| Jun/Aug 1998 | 350 | 58.7 | 10.3 | <0.001 |
| | 800 | 47.8 | 4.6 | |
| Apr/Jul 1999 | 350 | 43.2 | 5.2 | 0.246 |
| | 800 | 42.0 | 9.8 | |
| Dec 1999/Feb 2000 | 350 | 35.5 | 6.0 | 0.080 |
| | 800 | 36.8 | 4.2 | |

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**Table 3.** $CO_2$ deposition velocities ($V_d$; $mm\,s^{-1}$) as found with trees grown under the indicated $CO_2$ regimes derived as mean value from the quotient Exchange rate/concentration. Incubation under the indicated $CO_2$ concentration started in March 1998. Significance of differences of the $V_d$ mean values between 350 and 800 ppm growth regimes is 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.

| | $CO_2$ regime ppm | Mean $V_d$ $mm\,s^{-1}$ | SD | N | p-values |
|---|---|---|---|---|---|
| *Fagus sylvatica* | | | | | |
| Aug/Sep 1998 | 350 | 0.24 | 0.023 | 177 | <0.001 |
| | 800 | 0.07 | 0.006 | 135 | |
| Jun/Jul 1999 | 350 | 0.34 | 0.061 | 312 | <0.001 |
| | 800 | 0.17 | 0.025 | 246 | |
| Sep/Oct 1999 | 350 | 0.25 | 0.027 | 672 | <0.001 |
| | 800 | 0.07 | 0.009 | 213 | |
| *Quercus ilex* | | | | | |
| Jun/Aug 1998 | 350 | 0.25 | 0.038 | 288 | <0.001 |
| | 800 | 0.12 | 0.008 | 198 | |
| Apr/Jul 1999 | 350 | 0.38 | 0.041 | 338 | <0.001 |
| | 800 | 0.18 | 0.025 | 228 | |
| Dec 1999/Feb 2000 | 350 | 0.29 | 0.046 | 885 | <0.001 |
| | 800 | 0.15 | 0.014 | 567 | |

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**Table 4.** COS deposition velocities ($V_d$; mm s$^{-1}$) as found with trees grown under the indicated $CO_2$ regimes derived from linear model 1. Incubation under the indicated $CO_2$ concentration started in March 1998. Significance of differences of the $V_d$ values between 350 and 800 ppm growth regimes is indicated by p-values according to the linear model 2 (SAS Version 9.1). p-values > 0.05 indicate non-significant differences.

| | $CO_2$ regime ppm | $V_{d\,COS}$ (slope) mm s$^{-1}$ | N | p-values |
|---|---|---|---|---|
| *Fagus sylvatica* | | | | |
| Aug/Sep 1998 | 350 | 0.922 | 46 | 0.109 |
| | 800 | 0.646 | 45 | |
| Jun/Jul 1999 | 350 | 1.454 | 68 | 0.229 |
| | 800 | 1.253 | 82 | |
| Sep/Oct 1999 | 350 | 0.883 | 141 | 0.126 |
| | 800 | 0.787 | 71 | |
| *Quercus ilex* | | | | |
| Jun/Aug 1998 | 350 | 0.967 | 62 | 0.008 |
| | 800 | 0.761 | 66 | |
| Apr/Jul 1999 | 350 | 0.929 | 67 | 0.963 |
| | 800 | 0.926 | 76 | |
| Dec 1999/Feb 2000 | 350 | 1.538 | 194 | 0.002 |
| | 800 | 1.271 | 189 | |

**Table 5.** Carbonic anhydrase activities expressed in non-dimensional units (Wilbur and Anderson, 1948) as derived from the pH drops over time with and without enzyme as found with trees grown under the indicated $CO_2$ regimes. Incubation under the indicated $CO_2$ concentration started in March 1998. Significance of differences of mean values between 350 and 800 ppm growth regimes is 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; "nd" indicates no data.

| | $CO_2$ regime ppm | Mean CA activity | SD | N | p-value |
|---|---|---|---|---|---|
| *Fagus sylvatica* | | | | | |
| Aug/Sep 1998 | 350 | 4.90 | 0.96 | 9 | 0.968 |
| | 800 | 4.88 | 0.96 | 7 | |
| Jun/Jul 1999 | 350 | 5.32 | 1.07 | 9 | 0.311 |
| | 800 | 5.80 | 0.86 | 9 | |
| Sep/Oct 1999 | 350 | nd | | | |
| | 800 | nd | | | |
| *Quercus ilex* | | | | | |
| Jun/Aug 1998 | 350 | 17.8 | 5.2 | 9 | 0.589 |
| | 800 | 16.5 | 4.8 | 9 | |
| Apr/Jul 1999 | 350 | 18.6 | 7.7 | 10 | 0.087 |
| | 800 | 11.8 | 7.3 | 7 | |
| Dec 1999/Feb 2000 | 350 | 18.9 | 2.4 | 9 | 0.109 |
| | 800 | 16.9 | 2.6 | 9 | |

**Table 6.** Exchange of COS between the atmosphere and trees growing under normal and elevated $CO_2$ as described by the linear equations of the regression line (Model 1; Fig. 1) indicating the correlation between the initial COS concentration in the reference cuvette ($c_R$) and the exchange flux. Compensation points 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).

| Plant Species (Month/Year) | Growth regime | Equation linear regression | COS compensation point (95 % confidence interval) | |
|---|---|---|---|---|
| | | | nmol m$^{-3}$ | ppt |
| *Fagus sylvatica* (Aug/Sep 1998) | 350 ppm | $9.48 - 0.92 \cdot c_R$ | 10.28 (7.59–12.29) | 255 (188–305) |
| | 800 ppm | $5.40 - 0.65 \cdot c_R$ | 8.36 (0–12.78) | 207 (0–317) |
| *Fagus sylvatica* (Jun/Jul 1999) | 350 ppm | $12.93 - 1.45 \cdot c_R$ | 8.89 (4.90–11.60) | 220 (122–287) |
| | 800 ppm | $11.45 - 1.25 \cdot c_R$ | 9.14 (4.18–12.72) | 227 (104–316) |
| *Fagus sylvatica* (Sep/Oct 1999) | 350 ppm | $7.21 - 0.88 \cdot c_R$ | 8.17 (7.36–9.10) | 202 (183–226) |
| | 800 ppm | $8.95 - 0.79 \cdot c_R$ | 11.37 (6.33–15.20) | 282 (157–377) |
| *Quercus ilex* (Jun/Aug 1998) | 350 ppm | $8.75 - 0.97 \cdot c_R$ | 9.05 (6.71–10.96) | 224 (166–272) |
| | 800 ppm | $6.27 - 0.76 \cdot c_R$ | 8.24 (5.54–10.40) | 204 (137–258) |
| *Quercus ilex* (Apr/Jul 1999) | 350 ppm | $5.50 - 0.93 \cdot c_R$ | 5.92 (4.81–6.97) | 179 (119–173) |
| | 800 ppm | $12.33 - 0.93 \cdot c_R$ | 13.32 (10.14–16.02) | 330 (251–397) |
| *Quercus ilex* (Dec 1999/Feb 2000) | 350 ppm | $11.40 - 1.54 \cdot c_R$ | 7.41 (6.97–7.77) | 184 (173–193) |
| | 800 ppm | $13.79 - 1.27 \cdot c_R$ | 10.85 (9.35–12.09) | 269 (232–300) |

**Table 7.** Correlation (Pearson 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).

| Plant Species Year | Growth regime | $P_c$ | $R^2$ |
|---|---|---|---|
| *Fagus sylvatica* (Sep 1998) | 350 ppm | −0.858 | 0.736 |
| | 800 ppm | −0.585 | 0.342 |
| *Fagus sylvatica* (Jun/Jul 1999) | 350 ppm | −0.842 | 0.709 |
| | 800 ppm | −0.783 | 0.614 |
| *Fagus sylvatica* (Sep/Oct 1999) | 350 ppm | −0.954 | 0.910 |
| | 800 ppm | −0.786 | 0.619 |
| *Quercus ilex* (Jun/Aug 1998) | 350 ppm | −0.917 | 0.840 |
| | 800 ppm | −0.878 | 0.770 |
| *Quercus ilex* (May/July 1999) | 350 ppm | −0.981 | 0.962 |
| | 800 ppm | −0.917 | 0.841 |
| *Quercus ilex* (Dec 1999/Jan 2000) | 350 ppm | −0.968 | 0.938 |
| | 800 ppm | −0.763 | 0.582 |

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**Table 8.** 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 | $R^2$ | Type III SS – $CO_2$ | Type III SS – $CO_2 * c_R$ |
|---|---|---|---|
| *Fagus sylvatica* (Sep 1998) | 0.511 | 0.280 | 0.109 |
| *Fagus sylvatica* (Jun/Jul 1999) | 0.654 | 0.775 | 0.229 |
| *Fagus sylvatica* (Sep/Oct 1999) | 0.799 | 0.362 | 0.126 |
| *Quercus ilex* (Jun/Aug 1998) | 0.831 | 0.208 | 0.008 |
| *Quercus ilex* (May/Jul 1999) | 0.907 | <0.001 | 0.963 |
| *Quercus ilex* (Dec 1999/Jan 2000) | 0.884 | 0.182 | 0.002 |

**Table 9.** Estimates of global sink strength for carbonyl sulfide (COS) based on deposition velocity ($V_d$) ratios of COS versus $CO_2$ (for ranges see Tables 3 and 4). Net primary productivity (NPP) was calculated according to data published by Whittaker and Likens (1975) and Lieth (1975) and recalculated to NPP carbon according to Larcher (1994). For details see Sandoval-Soto et al. (2005). Estimates based on the linear model analysis are given for all ecotypes with *Quercus ilex* or *Fagus sylvatica* assigned as major species and are compared with those published by Sandoval-Soto et al. (2005).

| Ecosystem type | NPP $CO_2$ | $V_d$ ratios COS/$CO_2$ | | | $F_{COS}$ Tg a$^{-1}$ | | | Plant species related $V_d$ assigned Sandoval-Soto et al. (2005) |
|---|---|---|---|---|---|---|---|---|
| | $10^{15}$ g a$^{-1}$ | 350 ppm 2005 | 350 ppm This work | 800 ppm This work | 350 ppm 2005 | 350 ppm This work | 800 ppm This work | |
| Tropical rain forest | 60.34 | 1.7–3.6 | 1.7–3.6 | 1.7–3.6 | 0.246–0.508 | 0.246–0.509 | | *S. gabonensis. P. cladantha* |
| Tropical seasonal forest | 19.36 | 1.7–3.6 | 1.7–3.6 | 1.7–3.6 | 0.079–0.163 | 0.079–0.163 | | *S. gabonensis. P. cladantha* |
| Temperate evergreen forest | 10.49 | 1.5–2.9 | 2.4–5.3 | 5.1–8.5 | 0.037–0.071 | 0.060–0.130 | 0.055–0.091 | *Q. ilex, Q. agrifolia* |
| Temperate deciduous forest | 13.55 | 1.7–3.0 | 3.5–4.3 | 7.4–11.2 | 0.054–0.095 | 0.112–0.136 | 0.102–0.156 | *F. sylvatica* |
| Boreal forest | 15.49 | 1.0–1.7 | 1.0–1.7 | 1.0–1.7 | 0.036–0.063 | 0.036–0.063 | | *P. abies P. sylvestris* |
| Woodland and scrubland | 9.60 | 1.5–2.9 | 2.4–5.3 | 5.1–8.5 | 0.034–0.065 | 0.055–0.119 | 0.051–0.083 | *Q. ilex, Q. agrifolia* |
| Savannah | 21.78 | 1.5–2.9 | 2.4–5.3 | 5.1–8.5 | 0.076–0.148 | 0.125–0.270 | 0.115–0.189 | *Q. ilex, Q. agrifolia* |
| Temperate grassland | 8.71 | 2.0–3.0 | 2.0–3.0 | 2.0–3.0 | 0.041–0.061 | 0.041–0.061 | | *Z. mays, T. aestivum* |
| Tundra and alpine | 1.81 | 2.0–3.0 | 2.0–3.0 | 2.0–3.0 | 0.008–0.013 | 0.008–0.013 | | best guess |
| Desert and semi desert scrub | 2.61 | 1.5–2.9 | 2.4–5.3 | 5.1–8.5 | 0.009–0.018 | 0.015–0.032 | 0.014–0.023 | *Q. ilex, Q. agrifolia* |
| Extreme desert, rock, sand, ice | 0.12 | 1.0–3.0 | 1.0–3.0 | 1.0–3.0 | 0.000–0.001 | 0.000–0.001 | | best guess |
| Cultivated land | 14.68 | 1.3–3.8 | 1.3–3.8 | 1.3–3.8 | 0.043–0.130 | 0.043–0.131 | | *Z. mays, T. aestivum, B. Napus, P. sativum* |
| Swamp and marsh | 9.68 | 1.0–3.0 | 1.0–3.0 | 1.0–3.0 | 0.023–0.068 | 0.023–0.068 | | best guess |
| | | Total 1* | | | 0.686–1.404 | 0.843–1.696 | | |
| | | Total 2** | | | | 0.367–0.687 | 0.337–0.542 | |

* Total 1: sum of all rates according to Sandoval-Soto et al. (2005) and including the values adopted from the linear model 1.
** Total 2: only rates for ecosystems with the investigated tree species are taken into account.

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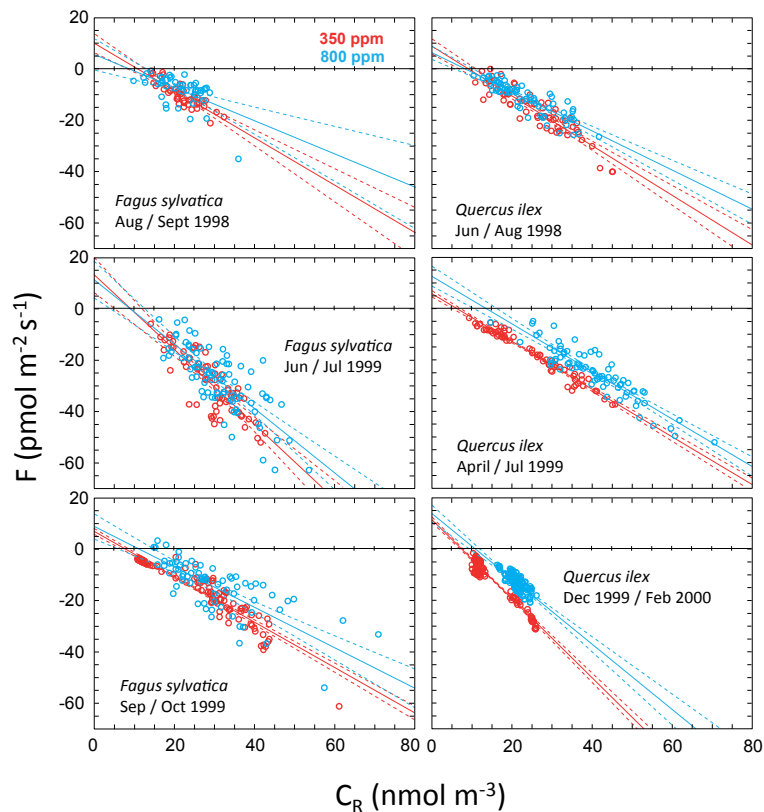
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Interactive Discussion

**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 March 1998 and measured at the indicated time periods. Given are the regression lines (continuous lines) together with their 95 % confidence bands (broken lines).