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Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere*

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Abstract. The flux of a trace gas between soil and atmosphere is usually the result of simultaneously operating production and consumption processes. The compensation concentration is the concentration at which the rate of production equals the rate of consumption so that the net flux between soil and atmosphere is zero. Production and uptake may be due to different processes, which are at least partially known for some of the trace gases, and which may be differently regulated. The direction and the magnitude of the flux between soil and atmosphere is a function of both the compensation concentration and the trace gas concentration in the ambient atmosphere. Compensation and/or ambient concentrations may fluctuate and thus may have a strong impact on the flux of CO, NO and NO_2, and to a smaller extent also on that of H_2. Compensation concentrations also exist for N_2O and OCS, but are too high to affect the flux under field conditions. Compensation concentrations have so far not been demonstrated for the flux of CH_4. However, the uptake of CH_4 by soil exhibits a threshold concentration below which no uptake occurs.

Introduction

Trace gases are minor constituents of the atmosphere, i.e. they occur at mixing ratios smaller than those of CO_2 (<350 ppmv). The global cycles of atmospheric trace gases are nevertheless of great concern, since their atmospheric abundance affects the physics and chemistry of the atmosphere and thus influences the climate on Earth (Crutzen 1983; Ramanathan et al. 1987; Prinn 1994). Changes in their sources or sinks may result in an increase or decrease of their atmospheric abundance. In fact, the concentrations of several atmospheric trace gases are presently changing (e.g. CH_4, CO, H_2, N_2O), while the reasons for these changes are not always clear (Rowland & Isaksen 1988; Prinn 1994). Many of these trace gases have cycles which are dominated or supported to a large extent by reactions in the biosphere, usually by exchange between atmosphere and soil (Andreae & Schimel 1989;

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Bouwman 1990). As it became clear that soils potentially affect the budgets of atmospheric trace gases, scientists started to study the fluxes of these gases. Since the eighties, reports on field measurements of trace gases exploded. Nevertheless, sources and sink strengths of most of the biogenic trace gases are still uncertain (Bouwman 1990; Prinn 1994). The more it is necessary to understand the mechanisms and the principles that are critical for the direction and the magnitude of the fluxes. In the following I will discuss one critical variable, the compensation concentration, and will give examples for the trace gases CO, H_2, N_2O, NO, NO_2, OCS and CH_4.

Definition of compensation concentration

The concept of the compensation concentration is based on the observation that production and consumption of a trace gas usually occur simultaneously in a soil and that the consumption rate is a function of the trace gas concentration, whereas the production rate is not. The compensation concentration is then the concentration at which the consumption rate reaches the same value as the production rate so that the result of both processes is zero flux.

For photosynthetic CO_2 assimilation by plants compensation concentrations are known from textbooks since quite some time. In this case, production and consumption of CO_2 is achieved by the same organism. In case of trace gases, on the other hand, production and consumption may be due to completely different organisms and may even involve purely chemical reactions. However, both production and consumption have to occur in the same soil sample, i.e. they have to be more or less homogeneously distributed within the entity that is investigated. For example, different vertical levels of soil may have different compensation points. The concept of compensation cannot be applied, however, if the production and consumption processes are spatially separated, e.g. production in deep soil and consumption in top soil.

In most cases, the effective concentration *in situ* of a trace gas is in a range where the uptake processes follow a pseudo first order reaction with respect to the trace gas concentration, i.e.

$$J = P - km \tag{1}$$

where J = flux between soil and atmosphere; P = production rate in soil; k = pseudo-first order uptake rate constant in soil; m = mixing ratio of the trace gas in the atmosphere.

However, the uptake process can also follow other kinetics, e.g. Michaelis-Menten kinetics

$$J = P - V_m m/(K_m + m) \tag{2}$$

where V_m maximum consumption rate in soil; K_m = Michaelis-Menten constant, i.e. m at which consumption rate equals 0.5 V_m.

As the compensation concentration m_c is reached at $J = 0$,

$$m_c = P/k \tag{3}$$

or

$$m_c = PK_m/(V_m - P) \tag{4}$$

Hence, the compensation concentration is a variable that contains the information of the magnitude of both the production process and the consumption process. Any environmental variable that affects either P or k (V_m, K_m) will also change m_c.

A change of m_c is critical for two reasons. First, it may affect the direction of the flux, and second, it may affect the magnitude of the flux. The direction of the flux is given by the relative magnitude of the compensation concentration with respect to the ambient concentration m_a. The flux is emission from the soil into the atmosphere if

$$m_c > m_a \text{since then } J > 0.$$

And vice versa, the flux is deposition from the atmosphere into the soil if

$$m_c < m_a \text{since then } J < 0.$$

A change of the direction of the flux may not only be the result of changing m_c, but also of changing m_a. Changes in the ambient concentration of a trace gas are likely for sites close to point sources such as automobiles emitting CO or NO, and are common for trace gases with a short residence time in the atmosphere (e.g. NO).

The magnitude of the flux is a function of the net production and the diffusion within the soil column. The resulting flux was modelled by Galbally & Johansson (1989) and is given by the following equation (Remde et al. 1993)

$$J = (m_c - m_a)\surd(k\delta D) \tag{5}$$

where δ = bulk density of the dry soil, and D = diffusivity of the trace gas in soil. It is evident that the magnitude of the flux increases with the difference between the compensation and the ambient concentration. Sensitivity analysis shows that the flux is especially dependent on the magnitude of k, which is contained in both m_c and the square root function (Remde et al. 1993).

The knowledge of the compensation concentration allows the calculation of the gross rates of production and consumption if either of the two is known in addition. Thus, a strategy to measure the compensation concentration usually allows to determine the flux as a function of the gross rates of both production and consumption.

Determination of compensation concentration

The compensation concentration in soil may be determined by different approaches depending on the type of compound and the analytical system available. Usually, the compensation points as well as the gross rates of production and consumption are determined by two different approaches.

The first approach directly measures the flux (J) as a function of the trace gas concentration (m). This is most conveniently done in an open system by flushing the headspace over the soil surface with a constant flow of air containing a defined concentration of the trace gas. The desired parameters can then be estimated from Eqs. 1–4. Alternatively, by plotting J against m, the compensation concentration (m_c) is given by the intercept with the x-axis, the gross production rate by the intercept with the y-axis, and k is given by the slope of the curve (Fig. 1).

The second approach uses a closed system and follows the trace gas concentration in the headspace with time until a constant value is reached (Fig. 2). This approach was used in early studies to measure the CO_2 compensation point in plants (Gabrielsen 1948). A constant compensation concentration is reached, if the gross rates of production and consumption are constant during the time of measurement. Then, the following equation is valid:

$$dm/dt = P - km \tag{6}$$

where dm/dt = the change of the concentration (mixing ratio) with time. The solution of the differential equation is obtained for the boundary conditions $m = m_o$ for $t = 0$, and $m = m_c$ for $t = \infty$ (Seiler 1978)

$$k = (1/t)\ln[(m_o - m_c)/(m_t - m_c)]. \tag{7}$$

The equation allows to determine the pseudo-first order uptake rate constant k from the experiment by regression of the concentrations measured at different time points and corrected for m_c to the above equation. The compensation concentrations m_c is obtained from the constant concentration that is finally reached at $t = \infty$. However, one should carefully check the possibility of confusing the compensation concentration with a threshold concentration

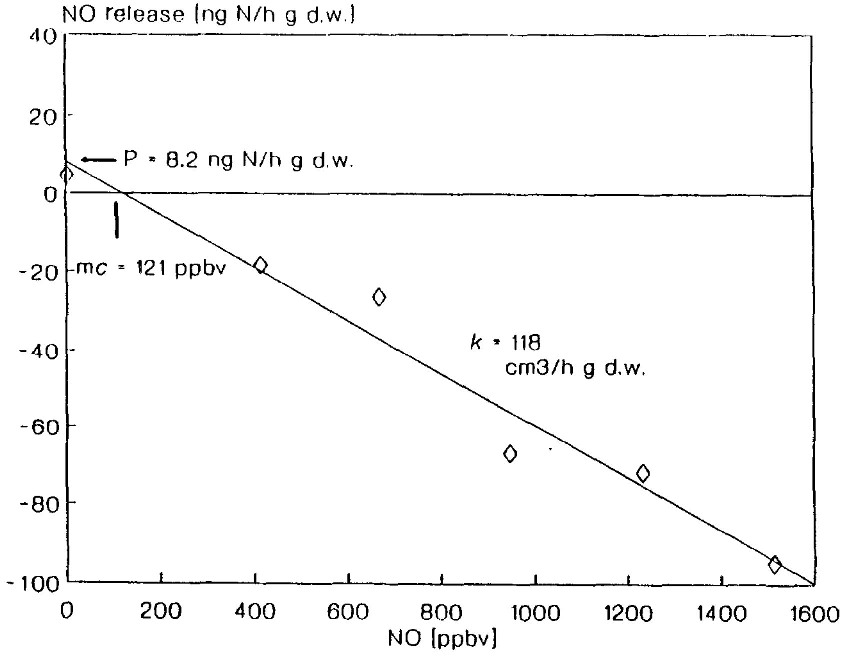

Fig. 1. Determination of the compensation point (m_c), the gross production rate (P) and the pseudo-first order uptake rate constant (k) by measuring the flux of NO as function of the NO concentration over soil in a flow-through system (adapted from Remde et al. 1993).

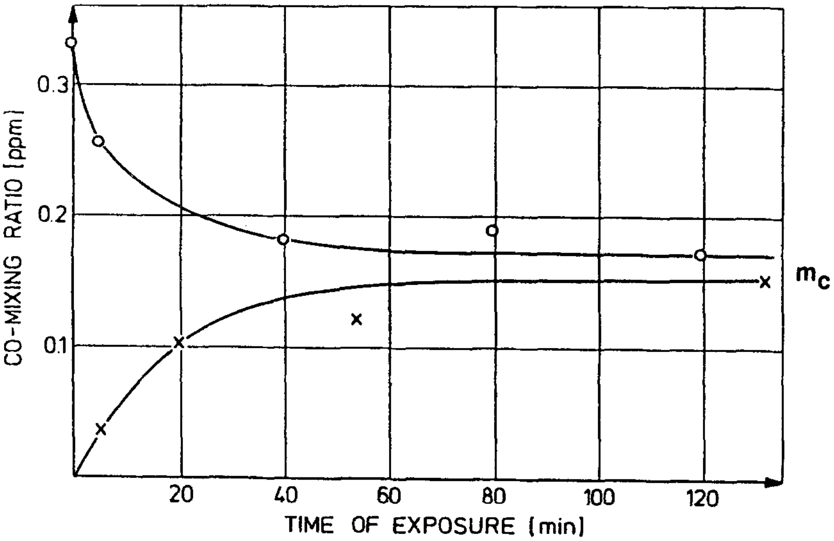

Fig. 2. Determination of the compensation point (m_c) by measuring the change of the CO concentration over soil in a closed system starting with either ambient CO (o) or zero CO (x) (adapted from Liebl & Seiler 1976).

(see below). Knowing k and m_c, the gross production rate P can be calculated by Eq. 3. In case of Michaelis-menten kinetics, Eq. 6 changes to

$$dm/dt = P - mV_{\max}/(m + K_m) \tag{8}$$

The parameters P, $V_{\max}$, and K_m can be obtained by numerical integration (Robinson & Characklis 1984), and m_c is calculated by Eq. 4.

Occurrence of compensation concentration

The existence of compensation concentrations has been demonstrated for the fluxes of CO, H_2, N_2O, NO, NO_2 and OCS. The existence of a compensation concentration was first discovered by Liebl & Seiler (1976) for the deposition of atmospheric CO. Using a static system, i.e. soil incubated in a vessel, the authors observed that the CO concentration finally reached a constant value which was the same whether the experiment was started with a CO concentration of zero or with ambient CO (Fig. 2). Obviously, CO was simultaneously produced and consumed. Similar results were later also reported for H_2, although in this case, the compensation concentrations were close to the detection limit of the analytical system (Seiler 1977).

This observation was later corroborated for field conditions (e.g. Conrad & Seiler 1980a; 1985a). There, the measurement of the compensation concentrations allowed to determine *in-situ* the rates of gross exchange of H_2 and CO between soil and atmosphere. The possibility to separately determine the gross rates of production and consumption allowed to study these rates as a function of environmental conditions and to conduct experiments designed to find out the processes underlying production and consumption rates.

In case of H_2, it was possible to show that H_2 production occurred in soils that were covered with N_2-fixing legumes, and that soils acted as a source for atmospheric H_2, when the biological N_2 fixation increased during the vegetation period (Conrad & Seiler 1980a). Furthermore, it could be shown that the consumption of H_2 was negatively affected by the increased H_2 production, an observation which was later explained by laboratory experiments demonstrating a reversible inhibition of the H_2-consuming soil enzymes by high H_2 concentrations (Conrad & Seiler 1981).

In case of CO, it was possible to show that the flux of CO changed with daytime both in magnitude and in direction due to the diel change in soil temperature (Conrad & Seiler 1985a; Scharffe et al. 1990). The change was dominated by the large activation energy of the CO production process which was due to thermal chemical decomposition of soil organic matter (Conrad & Seiler 1985b) resulting in much higher CO production at noon time than during night. The CO consumption, on the other hand, which was due to soil microorganisms (Conrad & Seiler 1980b), showed only a small apparent activation energy and a small diel rhythm (Conrad & Seiler 1985a).

The existence of compensation concentration was also shown for N_2O (Seiler & Conrad 1981). The mechanistic basis for compensation is quite plausible, since N_2O is an intermediate in the denitrification pathway and thus is potentially produced and consumed by the same microorganisms (Betlach & Tiedje 1981). However, the reduction of N_2O to N_2 was often found to tolerate less O_2 than the reduction of nitrate to N_2O (Tiedje 1988), so that a particular soil aeration status that favours N_2O production is usually less favourable for N_2O consumption. Indeed, the N_2O compensation concentrations were found to be much higher than the ambient N_2O concentration (Seiler & Conrad 1981). Under field conditions soils therefore probably generally act as a source for atmospheric N_2O. This conclusion is quite evident from the vast literature of N_2O fluxes which almost generally reports that soils act as a source for atmospheric N_2O (Bouwman 1990; Granli & Boeckman 1994). Fluxes of N_2O from the atmosphere into the soil have only rarely been reported (Ryden 1981; Slemr et al. 1984). Since N_2O concentrations in the atmosphere are quite stable, the compensation points for N_2O were in these reports obviously smaller than ambient. It is unknown, however, whether these low compensation points were due to a relatively low production or a relatively high consumption rate of N_2O in soil.

Compensation concentrations also exist for NO. Galbally & Roy (1978) observed that the NO mixing ratio within closed chambers increased only until a particular concentration was reached, presumably the compensation point. Later on, similar observations were made by Johansson & Granat (1984) and Slemr & Seiler (1984; 1991). The existence of NO compensation points was clearly demonstrated by laboratory experiments in which the NO flux was measured as a function of the NO concentration (Johansson & Galbally 1984; Remde et al. 1989). Using a flow-through system with defined NO concentrations, the compensation point can directly be measured by recording the NO mixing ratio at which the NO flux changes from release to uptake (Fig. 1). Under laboratory conditions it is relatively easy to control the concentration of NO over the soil, so that the compensation concentrations and the gross rates of NO production and consumption could be measured as a function of season (Baumgärtner & Conrad 1992a) or of soil variables, e.g. availability of O_2 (Krämer & Conrad 1991), soil moisture (Schuster & Conrad 1992) or temperature (Saad & Conrad 1993). In addition, the processes responsible for production and consumption of NO could be investigated (Conrad 1993a).

Under field conditions, however, NO fluxes in flushed chambers are usually not measured at defined but at ambient NO concentrations. Both the ambient NO concentration and the NO flux often fluctuate strongly, the flux even changing between emission and deposition. The data sets may allow to correlate the NO fluxes with the corresponding ambient NO concentrations and to derive an apparent NO compensation point. However, the data must be interpreted with care, as not only the ambient NO concentrations but also the soil conditions and thus the NO compensation point may change during the period in which the fluxes are measured. Using such field data, Slemr & Seiler (1991) determined NO compensation points on soil plots which were treated in different ways (fertilizers, vegetation, organic carbon). The study emphasized the importance to know the environmental regulation of compensation points in order to understand the dynamics of NO fluxes between soil and atmosphere.

With a similar data set Slemr & Seiler (1991) also determined compensation points for NO_x (consisting mainly of NO_2). In case of NO_2, chemical rather than microbial reactions seem to be involved in production and consumption of NO_2 (Baumgärtner et al. 1992).

Laboratory measurements of NO compensation points and NO uptake rate constants were used to calculate the NO flux under field conditions (Remde et al. 1993). Besides the knowledge of the difference between the compensation concentration and the ambient concentration of NO, it is necessary to know the NO uptake rate constant, the bulk density of soil and the diffusion coefficient of NO in the soil. For rough estimations, reasonable assumptions may be made for the latter two parameters. Remde et al. (1993) showed that the thus calculated fluxes agreed with the actually measured fluxes within a factor of 2 confirming the usefulness of the diffusional model developed by Galbally & Johansson (1989). These studies are so far the only ones determining trace gas fluxes *in-situ* from laboratory data of production and consumption activities. In principal, however, the model of Galbally & Johansson (1989) should also be applicable to other trace gases.

Since the net NO flux is driven by a concentration gradient between the soil and the free atmosphere, and since the gradient within the soil is the result of NO production and consumption reactions, the model of Galbally & Johansson (1989) predicts that compensation is reached in deeper soil layers. Most recently, we were able to show that this was actually the case and that the NO compensation concentration was reached at about 10 cm depth irrespectively of the NO concentration in the headspace (Fig. 3; Rudolph & Conrad, in prep.). This depth may be called compensation depth.

Until recently, the possible existence of compensation concentrations have almost generally been neglected when conducting field measurements of

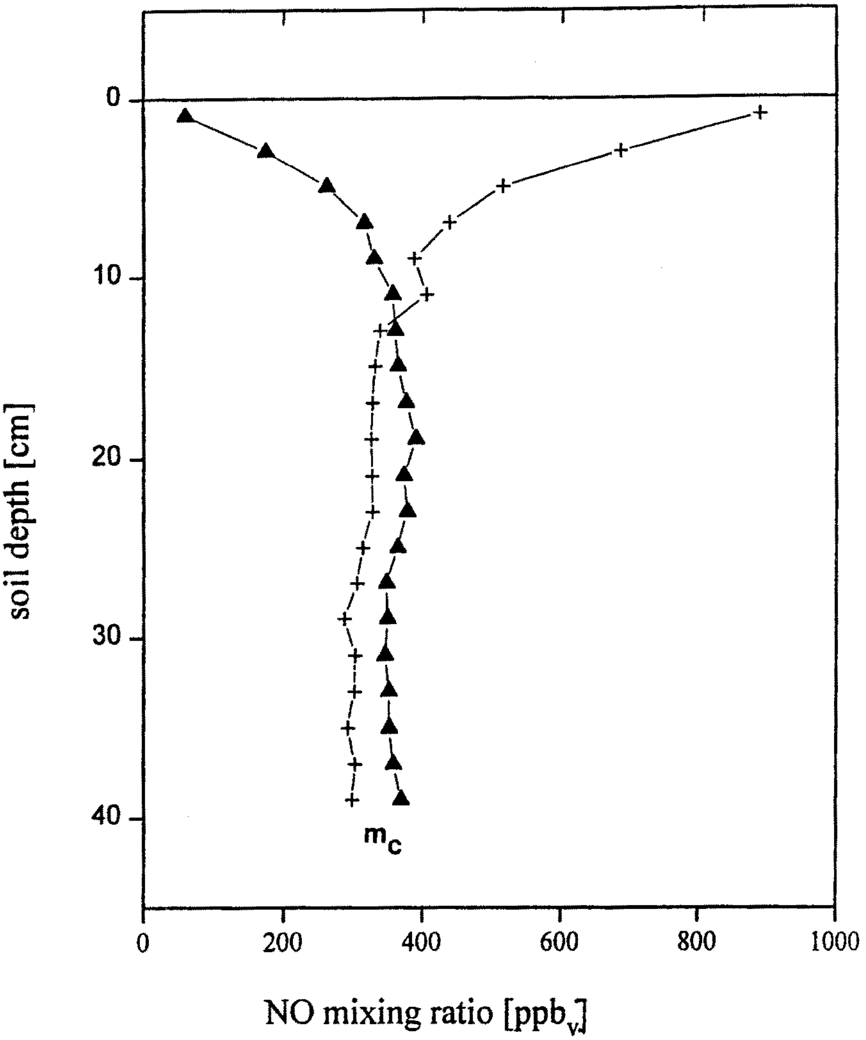

Fig. 3. Vertical profile of NO concentrations in the soil atmosphere of a soil core exposed to ambient (▲) or to elevated NO concentrations (+) (adapted from Rudolph, PhD thesis, Konstanz 1994).

reduced sulfur fluxes using chamber methods. Protocols to measure emission of DMS, COS and CS_2 from soils usually applied chambers flushed with zero gas, i.e. air or other carrier gases that contained none of the reduced sulfur compounds (Aneja et al. 1979; Adams et al. 1981; Goldan et al. 1987; Lamb et al. 1987; Hines & Morrison 1992). It is evident that under these conditions the direction of the flux must be an emission from the soil into the atmosphere.

By using ambient air concentrations Castro & Galloway (1991) showed that the flux indeed can change direction and result in a deposition of atmospheric OCS. Most recently, we were able to measure OCS compensation concentrations in laboratory experiments (Lehmann & Conrad, in prep.) using the same technique as for NO (Remde et al. 1989). The soils tested exhibited OCS compensation points on the order of 10–200 ppbv OCS, i.e. clearly higher than the ambient concentration of about 0.5 ppbv OCS. If OCS compensation points are similar under field conditions, the soils would generally act as a source for atmospheric OCS. In this case, field data of OCS fluxes are probably not strongly biased even when using zero gas for flushing chambers. The mechanisms of production and consumption of OCS are still very poorly understood (Bremner & Steele 1978; Kelly & Smith 1990), but seem to involve both chemical and microbial reactions (Lehmann & Conrad, in prep.).

For field conditions, all examples of compensation concentrations were so far sufficiently explained by assuming the simultaneous operation of a pseudo-first order uptake process in addition to a production process. The only case, where the uptake process had to be modelled by a Michaelis-Menten kinetic was the flux of NO between soil and atmosphere under completely anoxic conditions (Remde & Conrad 1991; Baumgärtner & Conrad 1992b). Here, production of NO is so high compared to NO uptake that the extrapolation of the compensation point by Eq. 3 gives only a virtual value which would grossly underestimate the real actual compensation point that has to be calculated from Eq. 4 (Fig. 4). It is unknown whether a situation such as depicted in Fig. 4 for completely anoxic conditions could realistically also occur under field conditions. However, the studies under anoxic conditions were useful in demonstrating that NO consumption in denitrifying soil and in soil microorganisms exhibited a remarkably high affinity for NO with K_m values in the order of <6 nM NO.

Possible confusion with threshold concentration

The concept of threshold concentration is based on the observation that the microbial consumption of a trace gas often stops at a particular concentration. The procedure for determination of threshold is given by this definition. Thus, thresholds can be determined by measuring the depletion of a trace gas in a closed system until a constant value is reached, i.e. the concentration at which utilization is no longer possible. However, the same procedure is often used to measure the compensation concentration (see above). It is therefore mandatory to check whether the final constance of the concentration is due to the inability to utilize the substrate (i.e. threshold) or is due to

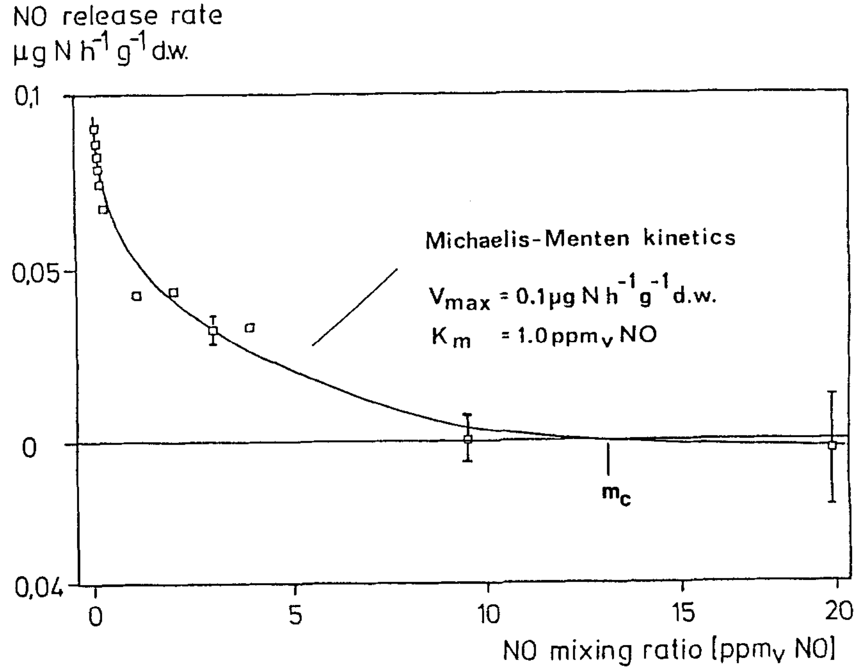

Fig. 4. Determination of the compensation point (m_c) and the Michaelis-Menten parameters of NO uptake by measuring the flux of NO release as function of the NO concentration over soil under anoxic conditions (modified from Baumgärtner & Conrad 1992b).

a dynamic equilibrium between simultaneous production and consumption (i.e. compensation concentration).

An example for the existence of a threshold concentration is found for the oxidation of atmospheric CH_4 by soil. The oxidation process at ambient CH_4 follows a pseudo-first order reaction (Whalen & Reeburgh 1990; Bender & Conrad 1993). However, below a particular concentration, the decrease of CH_4 slows down, and finally a concentration is reached at which CH_4 oxidation is no longer occuring (Fig. 5; Bender & Conrad 1993). This concentration is a threshold, since no CH_4 was produced in the soil, i.e. production could not be shown by incubating the soil under CH_4-free air.

In fact, CH_4 is so far the only biospheric trace gas for which the existence of a compensation concentration has so far not been shown. Soils generally seem to act as a sink for atmospheric CH_4. Only waterlogged soils, e.g. flooded rice fields, temporarily inundated wetlands, etc., are known to produce and emit CH_4 into the atmosphere (Bartlett & Harriss 1993; Sass 1994). Although some of the produced CH_4 is also oxidized at the oxic surface layer in these flooded soils, a compensation concentration does not exist in flooded soils, since CH_4

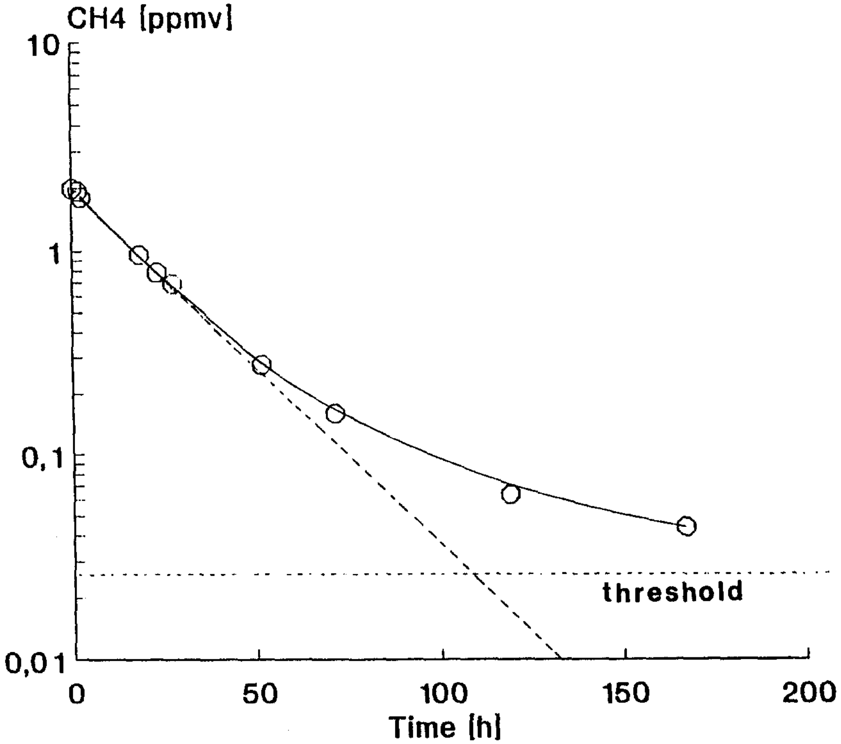

Fig. 5. Determination of the threshold of CH_4 uptake by soil in a time course experiment. No CH_4 production was observed when the soil was exposed to zero air (adapted from Bender & Conrad 1993).

production and consumption reactions are not homogenously distributed, but are localized in separate soil layers (Conrad 1993b).

However, occasional reports indicate that CH_4 may also be produced in aerated soils (Yavitt et al. 1990; Keller et al. 1990; personal communication by various colleagues). The production processes in these soils are so far unknown. The problem is not trivial, since the CH_4-producing bacteria are known to be strictly anaerobic, are relatively rapidly inactivated by exposure to O_2 and require reduced conditions for activity. Nevertheless, it may be found in future that some soils produce and consume CH_4 simultaneously and thus create a compensation concentration for CH_4. If the compensation concentration would be higher than the threshold of CH_4 oxidation and would be close to ambient CH_4 concentration, the kinetics of the turnover process and the resulting flux would probably form an equation that is more complex than observed for the other trace gases so far studied.

Table 1. Examplatory studies showing overlapping and non-overlapping ranges of ambient and compensations concentrations.

Trace gas	Ambient concentration [ppbv]	Compensation concentration [ppbv]	Reference
Overlapping ranges			
CO	70–170	<5–1200	Conrad & Seiler 1985
NO	<0.1–16	0.3–5.5	Slemr & Seiler 1991
NO_x	<0.1–24	<0.1–16.3	Slemr & Seiler 1991
H_2	500–700	<5–900	Conrad & Seiler 1979
Non-overlapping ranges			
OCS	0.5	10–200	Lehmann & Conrad in prep.
N_2O	310	ca.500	Seiler & Conrad 1981

Conclusion

Compensation concentrations are critical variables for the regulation of the flux between soil and atmosphere especially for those trace gases which fulfill the following criteria: (1) a dynamic change of compensation concentrations in soil and/or a dynamic fluctuation of ambient concentrations; (2) at least a partial overlap of the ranges of ambient and compensation concentrations (Table 1). These criteria are met by CO, H_2, NO and NO_2, which all show a relatively dynamic turnover in soil and in case of NO and NO_2 also have a short residence time (<1 day) in the atmosphere resulting in fluctuations of the ambient concentration. The trace gases N_2O and OCS apparently do not fulfill the necessary criteria. The ambient concentrations of both N_2O (residence time about 170 years) and OCS (residence time >1 year) are very stable and are significantly lower than the compensation concentrations so far determined.

Techniques measuring trace gas fluxes by chamber methods should account for the existence of compensation points. For example, chambers should not be flushed with zero-air, if the existence of consumption reactions has not been excluded. It may be tempting to use zero-air in order to avoid chemical reactions in the chamber atmosphere due to the introduction of O_3 or other reactive trace gases (Williamsen et al. 1992). However, there is a potential trade off which in the worst case would pretend a trace gas emission where actually a deposition takes place. The examples given above indicate that we better assume that a trace gas flux between soil and atmosphere is generally controlled by compensation until the opposite has been demonstrated.

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