Chapter 4

Surface Exchange

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4.1 Introduction

With surface exchange we mainly think of the dry flux of various chemical compounds between the terrestrial or aquatic surfaces of the earth and the overlying atmospheric turbulent boundary layer.

The fluxes can be upwards, *i.e.* from the surface to the air if the surface is the source of the compound. Examples are volatile organic compounds (VOCs) such as α-pinene emitted from plants or dimethylsulfide (DMS) deriving from algae living in the surface waters. The fluxes can also include particulate matter (aerosols) from either soil dust or sea spray.

The dry flux can also be downwards *i.e.* from the air to the surface. In this case the exchange is normally called deposition. Examples are air pollutants emitted from anthropogenic sources and then depositied from the air on the earth's surface. It could of course also be trace substances emitted from natural sources, or indeed compounds that are not emitted but created by air chemistry, such as ozone.

In EUROTRAC experimental data on surface exchange were obtained mainly in the sub-projects ASE and BIATEX plus some in TRACT (see volumes 4 and 9 in this series; Slanina *et al.*, 1997; Larsen *et al.*, 2000).

The primary effect of deposition is a cleansing of the air. The effect on the surface (*e.g.* plant communities or surface waters) can be harmful as, for example, in the case of ozone which is toxic to plants. In the case of deposition of nitrogen compounds or other nutrients the effect can be both beneficial and harmful. They can provide extra plant nutrients but, for example in estuarine areas, the extra nutrients can cause eutrophication, large growth of algae populations, and subsequent oxygen deficiency in the bottom waters when the dead algal material decomposes.

P. Borrell et al. (eds.), *Transport and Chemical Transformation of Pollutants in the Troposphere*

a. Wet deposition

When discussing deposition it is necessary, in addition to the turbulent dry flux to the surface, to include the amount that is deposited by precipitation. The significance of wet deposition depends on the climatic situation, but at Northern European temperate latitudes it provides about half of the atmospheric input of nitrogen to natural ecosystems.

(i) Wet-deposition methods to determine dry-deposition fluxes

Traditionally the "wet input" has been determined extensively, mainly because the collection of rainwater is quite simple. Indeed, because more complicated techniques are required for dry deposition measurements, wet deposition techniques have also been used for estimating dry deposition to forest canopies by putting rain water collectors on the forest floor. The excess concentration of chemical species in these collectors, compared with the concentration in collectors placed outside or above the forest is then taken to be the result of wash-off of material that has been dry deposited between rain events. The mehtod assumes that everything, which is dry deposited, is also washed off which is unfortunately not true for compounds absorbed in the leaf stomata. It also assumes that everything which is washed off, derives from dry deposition, which is not always the case because material on the outside of the leaves' cuticula can derive from the plant's interior.

With the advance of technology, we would recommend that this very approximate technique of determining dry deposition fluxes is abandoned all together. The errors are so large that they even may lead to wrong conclusions, apart from the fact that it only works for this (small) part of the surface that consists of permanent tall vegetation.

(ii) Determination of POPs by wet-deposition methods

This is not to diminish the role of wet deposition measurements as such. The wet input is large (at temperate latitudes it is about 50 % as mentioned above) and the sensitive analyses performed on collected rain water reveals deposition of "strange" compounds such as PCBs (polychlorinated biphenyls), chlorinated pesticides like Lindane (γ-isomer of hexachlorocyclohexane, or γ-HCH) and other persistent organic compounds (POPs).

The depositions are very low and cannot be measured with dry-flux techniques. However, the concentration of Lindane in rainwater has been determined at a number of Danish sites (remote from local sources) to be 27–122 ng/L during Spring and 7 ng/L in the remaining part of the year (Cleemann *et al.*, 1995). The variation from site to site was not significant. Hence this input must be assumed to originate from long-range transported material. The annual average including all sites was 15 ng/L corresponding to a deposition flux of 12 $\mu g/m^2$ per year. On a European scale these are not particularly high numbers. Thus Galassi (1987) reports concentrations up to 400 ng/L in rain water collected near Milan, Italy.

Nevertheless, 12 $\mu g/m^2$ extrapolated to the area of Denmark, including the coastal and inner Danish waters (1.25×10^5 km^2) gives 1.5 ton per year compared to annual sales of Lindane of between 8 and 15 tons in the corresponding years. To this figure we should probably add an additional portion resulting from dry deposition. Thus the input of Lindane to natural ecosystems is significant compared to the amounts used in the agricultural sector.

So this technique is of utmost importance in determining inputs to the ecosystems of less usual compounds. It also possesses a unique possibility of giving a longer term perspective on deposition and thereby an estimate of the then prevalent air concentrations of various atmospheric compounds. Here we think of the historical records preserved in for example the alpine glaciers. This aspect is dealt with in volume 5 in this series (Fuzzi *et al.*, 1997), and particularly in Gäggeler *et al.* (1997)

b. Plant physiology and dry deposition

If we now revert to dry surface exchange and concentrate on vegetated terrestrial surfaces, then it appears to be essential to consider the physiological state of the plant cover, at least for those compounds that are emitted or absorbed through the stomata of the plants. Thus the regulation of the emission/uptake is determined by the photosynthetic state of the plants. In the case where the emission/uptake is from the external surfaces of the leaves (cuticula) this plant physiological control may not be relevant. In the case of ozone it is both; while about half of the total dry flux depends on stomatal activity, the other half deposits on the outer surfaces or reacts with NO emitted from the soil (Pilegaard *et al.*, 1997), see section 4.2 below.

When the flux is dependent on stomatal activity, it is essential to have an indication of this in order to be able to parameterise the dry flux. Two significant indicators are the CO_2 flux and the water vapour flux which are both tracers of the plant activity. Large CO_2 downward fluxes and large evaporative losses generally go together to indicate that the stomata are open and thus favour deposition of certain compounds. However, a one to one correlation is not possible since CO_2 results from microbial activity and water vapour exchange also occur with the soil itself.

For a full parametrisation of the influence of plant physiology on the deposition process it is necessary to include a sub-model describing the plant's activity (CO_2 and water vapour exchange) as a function of external parameters such as solar radiation, temperature, air humidity, soil water content, season, *etc.*

4.2 Ozone deposition; the effect of NO emission from soil bacteria

Bacteria in the soil produce a number of intermediate compounds in the nitrification and denitrification processes. One is N_2O, although not very reactive and therefore not of interest in tropospheric chemistry, is a greenhouse gas and therefore of interest for other reasons. However, on the way to this compound some N remains as NO and is emitted as such to the atmosphere. NO is an active compound reacting with O_3 to make NO_2; chapter 2, section 2.2.a. In urban areas this is hardly of importance because of most of the NO is emitted from combustion or by traffic, but in rural areas, especially agricultural areas with application of large amounts of fertiliser, the ozone budget may be altered appreciably (Pilegaard *et al.*, 1997). The size of the NO input to the atmosphere is estimated to be 5–10 % of the anthropogenic emissions (Fowler *et al.*, 1997, p. 144) but the estimate is quite uncertain. However it is evident that, in air pollution studies on the regional scale, this effect cannot be ignored and that, in air-chemistry transport models, it is necessary to include land-use maps and data about the type of utilisation of the individual areas.

4.3 Emission of volatile organic compounds from plants

Vegetation synthesises a variety of hydrocarbon compounds that are not used in the plants own metabolism. The reason for this expenditure is not yet fully understood (Harborn, 1988). A fraction of the more volatile organic compounds (VOCs) produced is lost by evaporation and the ensuing emissions intervene in photochemical processes in the atmosphere.

Most of the VOC emission by plants passes through the stomatal openings of the leaves. Usually two main groups of VOCs are considered in vegetation emissions: isoprene and monoterpenes. Isoprene is mainly synthesised and emitted by broad-leaved-vegetation species while monoterpenes are the most frequent emission product from conifers.

a. Isoprene

Generally it is considered that isoprene is emitted exclusively through the plant stomata and that emission happens immediately, or in a short period, after isoprene synthesis within plant cells. Since there is no significant pool of isoprene inside the plant, emission rates are closely associated with the isoprene-biosynthesis rate and by variability in the resistance to diffusion to the ambient atmosphere associated with the degree of stomatal opening. As a consequence light intensity reaching the plant and leaf temperature are the two main environmental variables affecting and controlling isoprene emission fluxes on a short-term basis (hours–weeks). Isoprene emission fluxes vary rapidly with the daily solar cycle and decrease to insignificant values during night after the rapid exhaustion of reserves inside the plant. However sometimes the emission of isoprene has a delay of more than an hour depending on the environmental conditions. This type of behaviour suggests that, in some species such as *Quercus frainetto*, the biosynthesis of isoprene is not switched on until a primary pool of precursors is filled (Steinbrecher *et al.*, 1997a).

Algorithms have been developed and used with success to describe isoprene emission fluxes from vegetation. Isoprene emission is correlated with temperature and photosynthetically active radiation (PAR), with saturation at high temperatures and radiation intensities, following a pattern described by the Guenther model (Guenther *et al.*, 1993).

b. Monoterpenes

A large number of monoterpene compounds have been identified in emissions from vegetation, mainly conifers. The more common ones are α-pinene, β-pinene, limonene, myrcene, Δ^3-carene, camphene, 1,8-cineole and β-phelandrene (Guenther *et al.*, 1994). Monoterpene emissions are usually considered to be dependent mainly on temperature, and independent of light on the short-time basis. A large pool of monoterpene compounds is always present inside the trunk, branches and leaves, in quantities that depend only on the slow variation in the balance between loss from the plant and biosynthesis resulting from photosynthetic activity. Furthermore for these species the effect of light on monoterpene emission rates through the control of stomatal opening is also minor because the main resistance to monoterpene diffusion is in transport from terpene pools to the stomatal cavities, (Lerdau, 1991). The transfer rate is dependent on the monoterpene concentration in the pool and monoterpene characteristics such as diffusivity, solubility and vapour pressure. The emission flux of monoterpenes is often expressed as

$$F = F_0 \exp[c(T - T_0)] \tag{1}$$

referred to as the Guenther expression. This is equivalent to

$$\ln F = F_0 + c(T - T_0) \tag{2}$$

where F is the flux, T is the absolute leaf temperature, subscript zero refers to a reference state and c is an empirical dimensional constant. In other cases time expressions of the type

$$\ln F = \alpha + \frac{b}{T} \tag{3}$$

are given where a and b are empirical constants. These expressions are all variations on the Clausius-Clapeyron equation

$$\frac{e}{e_0} = \exp\left[\frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{4}$$

which describes the variation with temperature of the saturated vapour pressure e of a volatile compound (which is proportional to the concentration of the compound in the liquid phase inside the plant via Henry's law). L is the compound's heat of evaporation, R is the universal gas constant and subscript zero again indicates some reference state. Assuming saturated conditions inside the leaf cavities and a partial pressure in the ambient air of near zero, then the flux is

$$F = \frac{1}{r}(e - 0) = \frac{e_0}{r} \exp\left[\alpha \frac{T - T_0}{TT_0}\right] \tag{5}$$

where r is the resistance to transfer and $\alpha = L/R$. The quantity e_0/r can be identified as F_0.

In general this equation can be written:

$$\ln F = (\ln F_0 + \frac{\alpha}{T_0}) - \frac{\alpha}{T} \qquad (6)$$

from where the parameters a and b in equation (3) can be identified. If T is not too different from T_0, the parameter c in eqs (1) and (2) can be identified as $c = \alpha/T^2_0$. If furthermore $(T - T_0 << T^2_0)$, a linear expression can be obtained by expanding the exponential in eq. (5) (exp [ε] ≈ 1 + ε), viz.:

$$F = F_0[1 + \beta(T - T_0)] \qquad (7)$$

In contrast to isoprene, monoterpene emissions also occur at night, although the rate isusually lower than during the day because of the lower nocturnal ambient temperature. As a result of the different emission behaviour of isoprene and monoterpenes, the concentrations of isoprene in the ambient air above forested areas decrease significantly at night while the relative concentration of monoterpene is frequently higher during night-time periods (Torres *et al.*, 1997).

c. *Variations from the general pattern*

As previously mentioned, the general pattern of biogenic VOC emissions from vegetation do not represent the specific behaviour of every vegetation species in Europe and important deviations have been observed. Using laboratory screening to examine a large number of vegetation species, characteristic for northern as well as southern Europe, several studies have revealed that while most of the deciduous trees investigated always emit *traces* of monoterpene, a small percentage of deciduous tree species emit isoprene in *large* amounts (Steinbrecher *et al.*, 1997a; Pio *et al.*, 1997; Street *et al.*, 1997). The screening tests also showed that some conifers, such as Sylvester pine, Sitka spruce and Norway spruce, emit isoprène in addition to monoterpenes. In another atypical example some evergreen oak species, such as the Holm oak and Cork oak, which are common or predominant in Mediterranean regions, were found to be important emitters of monoterpene compounds, but not to emit isoprene.

Detailed studies performed, either in the laboratory using young specimen in controlled chambers, or in the field with adult specimen in natural ambient conditions, showed repeated clear differences in VOC composition. They also showed differences in emission rates between young and adult specimens, with young plants usually emitting at much higher rates than adult specimens (Street *et al.*, 1997; Pio *et al.*, 1997). These results raise questions about the accuracy of algorithms based on laboratory experiments with young trees only.

Both the absolute and relative amounts of monoterpenes emissions (magnitude and composition) change with leaf development. For example in Norway spruce monoterpenes emissions are low before bud burst and consist mainly of limonene and 1,8-cineole. When needles are fully developed α-pinene is the main compound emitted at a much greater emission rate (Steinbrecher *et al.*, 1997b).

In several conifer species not only temperature but also solar radiation influences monoterpene emission rates, again in contrast to the general picture given above. Norway spruce twigs located in the shadow crown may emit only at one tenth of the rate of similar twigs located in the sun at the same leaf temperatures. Experiments with ^{13}C tracer did not show any clear direct link between the monoterpene pool and monoterpenes emissions, indicating that, for these species, emitted monoterpenes originate primarily from direct photosynthetic products (Steinbrecher *et al.*, 1997b). Emission of monoterpenes by some evergreen broad leaf species, such as the holm oak, also shows a dependency on light and temperature with emission rates obeying the Guenther model (Kesselmeier *et al.*, 1996).

For conifer species emitting both monoterpenes and isoprene, the isoprene emission rate follows a daily emission pattern similar to that observed for emissions of isoprene from broad leaf plant species, with a strong dependence of emissions on solar radiation intensity and a smaller dependence on temperature. A similar behaviour was observed for eucalyptus trees, which predominantly emit isoprene at a strong rate during the day but also emit monoterpene compounds at a lower rate, day and night, with a predominant dependency on temperature (Street *et al.*, 1997; Pio *et al.*, 1997).

Although being predominant, leaves are not the exclusive source of biogenic VOC from vegetation. For example the cobs of Norway spruce emit eight different monoterpene compounds with a rate dependent on temperature. The contribution of cobs is only minor and constitutes about 2 % of the total plant emission. In contrast the trunks of Norway spruce are strong emitters of monoterpenes with rates that are quite variable from tree to tree. The trunks of undisturbed trees may contribute with up to 64 % to the total amount of α-pinene emitted by the spruce canopy (Steinbrecher *et al.*, 1997b). Injury to bark resulting in resin loss dramatically increases emission rates and changes the relative amounts of different monoterpenes emitted by coniferous species. The practice of resin tapping in coniferous forests increases monoterpene emissions by more than one order of magnitude (Pio *et al.*, 1997). Monoterpenes emissions from trunks are well correlated with temperature of bark and resin.

d. Other compounds

Some vegetation species also release other volatile organic compounds such as sesquiterpenes and oxygenated organic species (alcohols, organic acids, aldheydes and ketones). Much less is known about the emission flux characteristics of these compounds from vegetation than of isoprene and monoterpenes. Maize, which is a low emitter of isoprene and monoterpenes, emits important quantities of formaldehyde, acetaldehyde, acetone and acrolein from leaves and cobs (Street *et al.*, 1997). Spruce twigs release acetic and formic acid at rates which follow a typical daily pattern with maximum emissions during early afternoon (Kesselmeier *et al.*, 1997). Experiments with spruce, beech and ash showed the existence of seasonal effects with maximum organic acid emissions during fall when leaves start discolouring.

e. Conclusions

There have been large advances recently in our knowledge concerning the emission of VOCs by vegetation. However there is not yet a complete and precise view of the emission levels of the various compounds from the various plant species as a function of all the environmental variables controlling the emission processes. Factors such as inter-specimen variability within each species and seasonal variation, although recognised as important have not yet been fully quantified. Spatial and seasonal distribution of vegetation species and biomass density in the various European regions is still poorly known. As a consequence our present knowledge of biogenic VOC emissions to the atmosphere is still highly uncertain. Errors of as much as 500 % in the determination of emission fluxes have been estimated in US studies where biogenic emission inventories are very advanced (Simpson *et al.*, 1995; Lamb *et al.*, 1997).

4.4 Input of nitrogen and eutrophication of coastal waters

The atmospheric input of a pollutants and trace substances to the marine environment is of importance in policy development. Even in coastal areas the atmospheric input (wet and dry) can be of the same order as the riverine input, typically 30–40 % of the total load, and generally of the same order of importance regardless of the particular compound. Studies of nutrient input from the atmosphere to regional seas has become of special interest because of recent algae blooms in these waters (see for example Asman *et al.*, 1995). The knowledge of this and the processes behind has greatly improved as a result of the ASE subproject (Larsen *et al.*, 2000).

The interest in nutrient deposition derives from the environmental problems it can cause in terms of severe oxygen depletion induced by the decomposing algae. This happens in cases where the nutrient transfer is beyond what is beneficial for the aquatic ecosystem. The possibly beneficial thing about the atmospheric input is that it is in forms (like nitrate) that are readily available for biological uptake unlike organically bound nitrogen.

Other essential compounds of interest for the biological activity in the seas are completely dominated by the atmospheric input. Thus it is claimed that iron, the source of which is wind-blown dust from continental areas, is a limiting factor for the primary production in the Antarctic Ocean. It has even been hypothesised that this is a major factor in the oceanic carbon sequestration and thus of importance for the earth's climate (Martin *et al.*, 1994).

4.5 Emission from the coastal waters by spray formation

Breaking waves form spray. To a small extent some spray is emitted directly by wind action, but the most important mechanism is the entrainment of air into water. Bubbles are formed that rise to the surface and burst, ejecting droplets into the air. The larger droplets quickly gravitate out of the air again. However, the smaller droplets may stay airborne long enough to dry out and we are then left with an aerosol consisting of the material that originally was in solution in the water. For seawater this is mainly salt but the aerosol will also contain the pollutants and other trace materials present in the water.

When an air bubble rises through seawater it collects micro-organisms and other surface active materials on its surface and, when it breaks at the surface, the bubble film is thrown into the air as small droplets. Thus the composition of these droplets are not the same as in bulk seawater and enrichment factors of 500 are quite normal (Monahan and van Petten, 1989). Further enrichment of the particular substances can derive from fractionation by the living organisms before they are scavenged and thrown into the air. Recreation near the seashore may thus not be particularly healthy!

The spray production is an important process in the emission to the atmosphere of compounds dissolved in the ocean. Some emissions are of importance for the chemistry of the atmosphere: not only indirectly as a source of aerosols and condensation nuclei but also as a source of chemical compounds such as sulfates derived from biogases (*e.g.* dimethyl-sulfide, DMS). The subproject ASE has contributed significantly to the advancement of our knowledge in this field (Larsen *et al.*, 2000).

4.6 New developments in experimental techniques for flux measurements and future needs

The various methods for measuring surface exchange can roughly be divided into two categories: cuvette methods and micro-meteorological methods.

a. Cuvette methods

With the cuvettes a particular, relatively small, part of the surface is enclosed and then the concentration in the cuvette is monitored. If the cuvette is of the closed type, then the rate of change of the concentration is a measure of the flux. If the cuvette is of the flow-through type, the concentration difference between the inflow and outflow air is a measure of the flux.

One drawback of cuvette systems is that they interfere with what is to be measured since the exchange conditions inside the cuvette are artificial. Another problem can be absorption on the chamber walls. A final uncertainty is that the measurements require up-scaling to obtain area estimates. For example, with a small cuvette mounted on a twig or branch it is necessary to assume that the compound of interest only comes from twigs or branches and not from other parts of the canopy and that the area index of the active parts can be estimated. Part of this is also a sampling problem, namely to decide how many sampling spots are necessary to get a representative typical value.

Cuvette techniques are mainly interesting for estimating fluxes out of the soil or other specific compartments of the surface, for example for estimating the relative importance for the total exchange of the various parts of the plants.

b. Micro-meteorological methods

Micro-meteorological methods on the other hand do not in principle interfere with the emission/deposition conditions, and because of the turbulent diffusion between the upstream surface and the level of measurements, the measured flux is an area average. The area from which the measured surface exchange has taken place is known as the "footprint". Its size depends on the height of the measurements and the level of turbulence, which in turn can be expressed as a function of the surface roughness and the atmospheric stability.

There are some basic conditions that must be fulfilled for all micro-meteorological methods. First the flow and chemical fields must be stationary; for instance if the mean concentration C changes with time, the estimated flux is not equal to the required surface flux. Secondly the underlying terrain must be flat, with homogeneous plant cover in the footprint area; otherwise there will be horizontal advection, and again the estimated flux will deviate from the required surface flux. If the an emission flux is being measured, a special problem can occur in night-time stable conditions on a sloping terrain. Here catabatic flows can carry the emissions away under the micro-meteorological flux level. It is a known phenomenon for night-time CO_2-flux measurements over forests.

c. The profile method

There are two classical methods for flux determination in micro-meteorology: the profile method and the eddy-correlation method.

The profile method in its simplest form uses the mean concentration difference between two levels. To convert this into a flux requires a model for the exchange coefficient (eddy diffusivity). It can for example be obtained from surface-layer-similarity theory using empirical functions of the Monin-Obukhov length. Alternatively it can be obtained by measuring the concentration difference of another scalar for which it is possible to determine the flux independently. Thus

$$F_1 = F_2 \frac{\Delta C_1}{\Delta C_2} \tag{8}$$

where F_1 is the flux to be determined and F_2 is the known flux, and ΔC_1, ΔC_2 are the mean concentration differences. A slightly rough but very robust estimate can be obtained by using momentum for the "known scalar". A disadvantage of the method is that it requires very long homogeneous fetches because the height of observation must be relatively large for similarity theory to be valid (one to two orders of magnitude larger than the aerodynamic surface roughness - a problem for observations over forests). Another consequence is that the footprints of the two measurement levels are different.

d. Eddy correlation methods

The eddy-correlation method on the other hand does not suffer from any of these limitations. It requires no assumptions or empirical input but gives the flux directly. It is the preferred method. The only constraint is that the level of measurements must be sufficiently away from local roughness elements such that the mean flow streamlines are reasonably straight. However, if the scalar spectrum contains very low frequency fluctuations, the flux calculation procedure becomes very sensitive to the external alignment of the sonic (rotation of the co-ordinate system in order to make the mean vertical velocity $\bar{w}$ equal to zero). This also depends on the choice of the length of the averaging time.

This potential error can become very large if this procedure is neglected. The fluxes can become lost altogether if a levelling instrument is placed near the sonic while still neglecting the alignment procedure: the only effect of the "inclinometer" is to distort the streamlines through the anemometer more than they otherwise would be. In Fontan *et al.* (1997) it is claimed that the low frequency variations in the scalar spectrum should be removed before computing the eddy correlation in order to avoid spurious fluxes. We doubt that this conclusion can be made if a proper alignment procedure is followed.

The disadvantage of the eddy-correlation method is that it requires rapid response sensors. While this is no problem for the determination of the vertical wind speed fluctuations using a sonic anemometer, a suitable analyser for the scalar concentration fluctuations does not exist for many compounds.

e. Analysers for use in flux measurments

Analysers using chemiluminescent techniques with response times well under one second exist for O_3, NO_2 and NO. For CO_2 and water vapour, which has high concentrations in the atmosphere compared to trace elements, it is possible to utilise infrared absorption spectroscopy. A new detector utilises solid state laser diodes (see Bösenberg *et al.*, 1997) tuned to an absorption band characteristic for the molecule of interest. However, to keep the tuned frequency stable the emitter and detector must be kept at a very precise cryostatic temperature. Thus in practice the apparatus is quite complex, not very rugged, expensive, and each apparatus is able to detect only one particular compound. However improvements can soon be expected.

FTIR (Fourier transform infra red) spectroscopy is another optical method that has been applied in flux measurements of atmospheric gases. In this technique a atmospheric broad-band infrared absorption spectrum is analysed and a large number of interesting compounds like N_2O, CO_2, CO, CH_4, H_2O, NH_3 *etc.* can be measured simultaneously with good specificity. By using long optical path lengths (100–1000 m) and sophisticated multi-regression evaluation algorithms, detection limits of the order of a few ppb (10^{-9} volume per volume) can be obtained. Long optical path lengths can be obtained either by applying closed multi-reflection cells, or open long-path systems. In the latter application the additional advantages of integration along the path length, and non-intrusive measurements are achieved. Because the time resolution in the measurements is limited, the technique has mainly been applied in profile or cuvette measurements. An advantage with the spectroscopic techniques is that accurate difference measurements can be made by taking the ratio of the spectra to be compared. Thus all instrument factors and common concentrations errors cancel leaving only a spectrum of the concentration differences. With this technique differences less than 1/1000 of the ambient concentrations can be detected and it has been applied in profile measurements and Relaxed Eddy Accumulation measurements (see below) of greenhouse gas fluxes.

Another successful application of FTIR spectroscopy is flux measurements using tracer gas release techniques. A known flux of a synthetic trace gas is released from the area under study, and by measuring simultaneously the trace gas and the gas under study the flux of the latter may be determined. This technique has been applied to studies of the emission of ammonia from liquid manure spreading and emissions of methane from waste depositories.

f. Relaxed eddy accumulation

A relatively new technique which may have a lot of potential, is the so-called Relaxed Eddy Accumulation (REA) technique. In its simplest form it consists of a pump, a fast two-way valve, and two collector reservoirs (for example teflon bags), together with a sonic anemometer to control the valve. When the air motion is upwards, air is led to the "up" reservoir and *vice versa*. After a suitable period of time (say 30 min.), the concentrations in the two reservoirs of all components of interest can be determined by using conventional slow response analysers. The flux is then determined from

$$F = \beta \sigma_w (C_+ - C_-) \tag{9}$$

where C_+ and C_- are the concentrations in the "up" and "down" reservoirs respectively, σ_w is the standard deviation of the fluctuations of the vertical wind velocity, w, and β is an empirical coefficient of order one. It is not a constant though, but depends on the statistical properties of the turbulence and thus indirectly upon the stability).

There are many variations to the actual design. On-line analysers can replace the bags and analysers based on a differential principle are ideal. Introducing an interval for w (a so-called dead band) in which air is not sampled in either of the reservoirs has the advantage of reducing the activity of the valve (better life time) and increasing the difference between C_+ and C_-. If the dead band is determined as $\pm 1/2\ \sigma_w$, β turns out to be 0.42 independent of atmospheric stability (Jensen *et al.*, 1998).

If the compounds of interest are very reactive, one may *not* want them to pass through the pump and valve before detection. In this case a design could be used as shown in Jensen *et al.* (1998), built to measure VOC fluxes or fluxes of NH_3.

In their requirements for chemical analysis REA systems are similar to those required when using mean profile or gradient techniques. The advantages of REA is that, just like the eddy-correlation method, no assumptions are made concerning similarity profiles and that it has a well defined footprint.

4.7 Conclusions

During the lifetime of EUROTRAC there has been much development in our experimental capability to measure the exchange of chemical compounds between the atmosphere and the natural surfaces, terrestrial or aquatic and this has led to a significant increase in our knowledge base of the magnitude of these fluxes. Prior to BIATEX and ASE not even the sign of many of these fluxes was known. In turn the data have been used to validate and improve parametrisation schemes or construct new ones and, in some cases, have given an impulse to the development of completely fresh theoretical ideas about how to treat the physical/chemical processes involved. Despite of the large steps made in this direction more work, both experimental and theoretical, is unfortunately still needed, before we can be satisfied that our descriptions of biogenic emissions and deposition to the biosphere are good enough to be include with confidence in the models used for policy development.

4.8 References

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