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^{222}Rn flux and soil air concentration profiles in West-Germany. Soil ^{222}Rn as tracer for gas transport in the unsaturated soil zone

By HELMUT DÖRR and KARL OTTO MÜNNICH, *Institut für Umweltphysik, University of Heidelberg, Im Neuenheimer Feld 366, 6900 Heidelberg, FRG*

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ABSTRACT

Measurements of the ^{222}Rn activity concentration profile in the soil and the ^{222}Rn flux in West-Germany are presented. The spatial pattern of the ^{222}Rn flux depends more on soil type than on the ^{226}Ra activity of the soil material. The average ^{222}Rn flux from sandy soils is 1000–2000 dpm m^{-2} h^{-1} and 4000–6000 dpm m^{-2} h^{-1} from loamy and clayey soils. Weekly ^{222}Rn flux measurements during a period of 1 year at a sandy site show no significant temporal variations. At a clayey site, the ^{222}Rn flux tends to be higher in summer than in winter. The permeability coefficient P_{Rn}, obtained from simultaneous ^{222}Rn flux and concentration profile measurements in various soils, can be expressed as a function of the soil parameters total porosity ε_0, soil moisture F, tortuosity k and the molecular diffusion coefficient D_0 of ^{222}Rn in air: $P = D_0((\varepsilon_0 - F)/k - \text{const.})$. The flux of any other gas into or out of the soil can thus be calculated from its measured concentration profile in the soil and from the ^{222}Rn permeability coefficient, replacing the molecular diffusion coefficient of ^{222}Rn by that of the specific gas under consideration. As an example, this method of flux determination is demonstrated for the soil CO_2 flux to the atmosphere and for the flux of atmospheric CH_4 into the soil.

1. Introduction

The radioactive noble gas ^{222}Rn ($t_{1/2} = 3.8$ d) is produced by α-decay of ^{226}Ra ($t_{1/2} = 1600$ d), a trace component of all soils. Only a small fraction of totally produced ^{222}Rn escapes from soil particles into soil air depending on the specific soil particle surface and, thus, on grain size distribution. Gas transport in the unsaturated soil zone is by molecular diffusion. The ^{222}Rn flux at the soil surface depends on the ^{226}Ra content, grain size distribution and on the diffusion resistance of the unsaturated soil zone.

In this paper, we present directly measured ^{222}Rn fluxes and soil air concentration profiles in West-Germany and discuss the use of ^{222}Rn as tracer for gas transport in the unsaturated soil zone. To use ^{222}Rn as tracer for soil gas transport means to calculate trace gas fluxes at the soil surface from their soil air concentration profile and the permeability ("diffusion coefficient of gas in the soil") obtained from simultaneously measured ^{222}Rn flux and concentration gradient. As an example, we discuss the determination of the soil CO_2 flux into the atmosphere and the flux of atmospheric methane into aerated soils and compare the "^{222}Rn calibrated" with directly measured fluxes.

2. Experimental

Soil air samples were taken by driving connectable, stainless steel tubes (1 m long, 6 mm outer and 2 mm inner diameter) into a preset depth. Soil gas inlet is through 8 holes (0.5 mm diameter) just behind the cone tip. For ^{222}Rn, CO_2 and CH_4 measurement, 200–300 ml soil gas

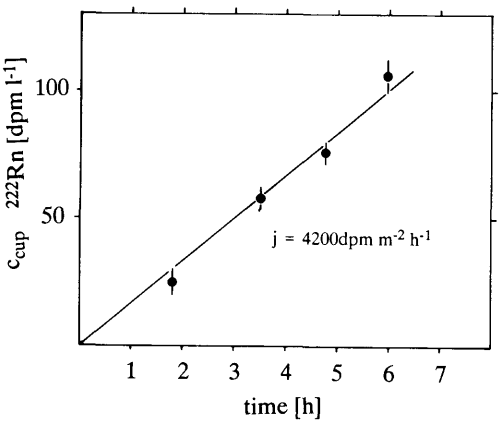

Fig. 1. Example of a direct flux measurement in the Botanical Garden of Heidelberg University: concentration increase with time under an inverted cup. The flux is calculated from the slope of the linear regression line and height of the inverted cup of $h = 24$ cm. The corresponding ^{222}Rn concentration profile is shown in Fig. 2c.

is sampled at a flow rate of ~ 400 ml min^{-1}. Soil gas fluxes were measured directly by the inverted cup method. The concentration change under a tin container (25 cm height, 0.25 m^2 cross-section) was measured after an accumulation period of 30 min to 1 h. The rim of the container was driven ~ 5 cm into the soil. Fig. 1 shows an example of the ^{222}Rn concentration increase under an inverted cup with time. The ^{222}Rn flux is calculated from the slope of the linear regression and the height of the container (cf. eq. (6)) to be $j_0 = 4200$ dpm m^{-2} h^{-1} in this example (1 dpm m^{-2} h^{-1} = $2.2 \cdot 10^{-4}$ atoms cm^{-2} s^{-1}).

The samples were taken in pre-evacuated glass flasks and alternatively in air bags made of plastic-covered aluminum foil (hostaphan–aluminum–PE foil, Kalle, Wiesbaden, FRG). Gas inlet is through a one-way teflon stop-cock (P.v. Berg, Kirchseeon, FRG).

^{222}Rn activity was measured in slow-pulse ionization chambers (Roether and Kromer, 1978). With a glass syringe, 100 ml of soil gas were injected into the ionization chamber which is filled with 1.5 l argon as counting gas. The reproducibility of ^{222}Rn activity measurement is typically $\pm 5\%$. Soil CO_2 concentration was measured with a non-dispersive infrared gas analyzer (NDIR, URAS 1) after diluting the sample with N_2 in a standard manner (Barth, 1980). The reproducibility of CO_2 measurement is $\pm 6\%$. Methane concentration is measured by gas chromatography (Born, 1988; Born et al., 1990).

3. Theoretical considerations

Diffusional transport of a gas through porous media is described by Ficks law no. 1:

$$j = -P \nabla c, \tag{1}$$

where j is the flux density and c the concentration of the gas under consideration; $P = SD$ is the permeability; S is the "solubility", i.e., the equilibrium partition factor between the medium in question and a reference medium; D is the diffusion coefficient of the gas in the medium. If diffusion of a gas in the unsaturated soil zone is considered, the obvious reference medium is soil air, which makes $S = \varepsilon$, the air filled fraction of the total soil volume (available porosity). The available porosity ε can be expressed as the difference between total porosity ε_0 and the volumetric soil moisture content F, i.e., $\varepsilon = \varepsilon_0 - F$. The diffusion coefficient in the unsaturated soil zone D is given by $D = D_0/k$, where D_0 is the molecular diffusion coefficient in air and k is the tortuosity. The tortuosity describes the higher diffusion resistance due to variation of diffusion cross-section in the soil by soil grains and water-filled capillary regions (bottle necks). The permeability P can thus be expressed as a product of the molecular diffusion coefficient D_0 and a function of soil parameters

$$P = D_0(\varepsilon_0 - F)/k. \tag{2}$$

Assuming homogeneity in the x- and y-directions, the change of ^{222}Rn concentration in soil air with depth z and time is described by the diffusion eq.:

$$\frac{dc}{dt} = D \frac{d^2 c}{dz^2} + Q - \lambda c, \tag{3}$$

where $\lambda = 2.1\ 10^{-6}$ s^{-1} is the ^{222}Rn decay constant and Q the ^{222}Rn source strength normalized to a unit soil air volume. Assuming a homogeneous ^{222}Rn source strength Q_0 and a depth-independent diffusion coefficient D, the steady state ($dc/dt = 0$) ^{222}Rn concentration profile is obtained by solving eq. (3) with the boundary

conditions $c(z=0)=0$ and $(\mathrm{d}c/\mathrm{d}z)_{z\to\infty}=0$ (z is taken positive in the downward direction):

$$c(z)=c_\infty(1-\exp(-z/\bar{z})), \tag{4}$$

where (4a) $\bar{z}=\sqrt{D/\lambda}$ is the relaxation depth, and (4b) $c_\infty=Q_0/\lambda$ is the concentration at depth $z\gg\bar{z}$, where steady state between ^{222}Rn production and radioactive decay is reached and diffusional loss of ^{222}Rn can be neglected. Note that c_∞ is not the equilibrium activity between ^{222}Rn and ^{226}Ra, because most of the produced ^{222}Rn decays within the soil grains. The fraction of ^{222}Rn that escapes from soil particles by α recoil and diffusion (Rama and Moore, 1984) is of the order of 1–10% depending on the effective soil particle surface and, thus, on grain size distribution. The fraction f of emanating ^{222}Rn is given by (4c) $f=c_\infty/c_{\mathrm{Ra}}\,\varepsilon/\rho_{\mathrm{b}}$, where c_{Ra} is the ^{226}Ra concentration of soil material and ρ_{b} is the soil bulk density ($\varepsilon/\rho_{\mathrm{b}}$ is the conversion factor between soil gas volume and soil particle mass).

The relaxation depth $\bar{z}$ is calculated from $\bar{z}=\sqrt{D_0/(k\lambda)}$ to be $\bar{z}=185$ cm and $\bar{z}=138$ cm, assuming tortuosities of $k=1.4$ and $k=2.5$, respectively (Carman, 1956; Penman, 1940).

The ^{222}Rn flux density at the soil surface is obtained from eq. (1) by inserting eq. (4), so that:

$$j_0=-Pc_\infty/\bar{z}, \tag{5}$$

where c_∞ and $\bar{z}$ have to be determined from the concentration profile and the permeability P has to be known.

The ^{222}Rn flux density at the soil surface can alternatively be measured directly from the concentration increase with time under an inverted cup placed above the soil surface. The flux density is calculated from

$$j_0=\frac{\Delta c}{\Delta t}H, \tag{6}$$

where Δc is the concentration increase during Δt and H is the height of the inverted cup. Simultaneous measurement of the ^{222}Rn flux at the soil surface and the ^{222}Rn concentration profile in soil air gives the permeability $P=-j_0/\mathrm{grad}\,c=j_0\,\bar{z}/c_\infty$ (cf. eqs. (1) and (5)).

Likewise, the permeability P is obtained from only one ^{222}Rn concentration measurement at a depth l, where the exponential profile can be assumed as linear ($l<\bar{z}$) and the ^{222}Rn flux: $P=j_0/(c(l)/l)$.

The concentration profile of any other, non-radioactive gas in the unsaturated soil zone is obtained from eq. (3) by setting $\lambda=0$ and inserting the proper depth distribution of the source or sink strength Q. The source strength of soil CO_2 which is produced by microbial decomposition of soil organic material and root respiration and the sink strength of methane which is microbially decomposed in aerated soils, can be assumed to decrease exponentially with depth due to an exponential decrease of root density, soil organic material and micro-organism population density:

$$Q(z)_{\mathrm{CO_2}}=Q_{0,\mathrm{CO_2}}\exp(-z/z_{\mathrm{CO_2}}) \tag{7a}$$

$$Q(z)_{\mathrm{CH_4}}=-Q_{0,\mathrm{CH_4}}\exp(-z/z_{\mathrm{CH_4}}). \tag{7b}$$

The steady-state solution of eq. (3) with the boundary conditions $c(z=0)=c_{\mathrm{atm}}$ and $(\mathrm{d}c/\mathrm{d}z)_{z\to\infty}=0$ (CO_2 production and CH_4 decomposition is negligible in depths where the organic matter content approaches zero) is

$$c(z)_{\mathrm{CO_2}}=c_{\infty,\mathrm{CO_2}}(1-\exp(-z/z_{\mathrm{CO_2}}))+c_{\mathrm{atm}} \tag{8a}$$

$$c(z)_{\mathrm{CH_4}}=c_{0,\mathrm{CH_4}}\exp(-z/z_{\mathrm{CH_4}})+c_{\infty,\mathrm{CH_4}}, \tag{8b}$$

where c_{atm} is the CO_2 concentration at the soil surface, $c_{\infty,\mathrm{CO_2}}=Q_0 z_{\mathrm{CO_2}}^2/D$ the difference between the CO_2 concentration at depth $z\gg z_{\mathrm{CO_2}}$ and the atmospheric CO_2 concentration; $c_{0,\mathrm{CH_4}}$ is the difference between the methane concentration at the soil surface and the concentration c_∞ at depth $z\gg z_{\mathrm{CH_4}}$. The relaxation depth $z_{\mathrm{CO_2}}$ and $z_{\mathrm{CH_4}}$ is given by the depth distribution of the soil CO_2 source and methane sink strength, respectively. The CO_2 and methane flux at the soil surface is obtained from eqs. (1) and (8a, b) as:

$$j_{0,\mathrm{CO_2}}=-P_{\mathrm{CO_2}}c_{\infty,\mathrm{CO_2}}/z_{\mathrm{CO_2}}, \tag{9a}$$

$$j_{0,\mathrm{CH_4}}=P_{\mathrm{CH_4}}c_{0,\mathrm{CH_4}}/z_{\mathrm{CH_4}}. \tag{9b}$$

$P_{\mathrm{CO_2}}$ and $P_{\mathrm{CH_4}}$ are the permeabilities of CO_2 and methane, respectively.

The $CO_2/^{222}$Rn and $CH_4/^{222}$Rn flux ratios, obtained from eqs. (9a), (9b), (2) and (5), do not depend on soil parameters:

$$J_{\mathrm{CO_2}}/j_{\mathrm{Rn}}=D_0^{\mathrm{CO_2}}/D_0^{\mathrm{Rn}}\,c_{\infty,\mathrm{CO_2}}/c_{\infty,\mathrm{Rn}}\,\bar{z}/z_{\mathrm{CO_2}}, \tag{10a}$$

$$J_{\mathrm{CH_4}}/j_{\mathrm{Rn}}=-D_0^{\mathrm{CH_4}}/D_0^{\mathrm{Rn}}\,c_{0,\mathrm{CH_4}}/c_{\infty,\mathrm{Rn}}\,\bar{z}/z_{\mathrm{CH_4}}. \tag{10b}$$

The ratio of the molecular diffusion coefficients is constant at a given temperature ($D_0^{\mathrm{CO_2}}/D_0^{\mathrm{Rn}}=1.3$, $D_0^{\mathrm{CH_4}}/D_0^{\mathrm{Rn}}=1.8$ at 15°C). The CO_2 and CH_4 fluxes at the soil surface are

calculated from eqs. (10a) and (10b) using measured CO_2, CH_4 and ^{222}Rn concentration profiles and the directly measured ^{222}Rn flux.

All equations are derived under the assumption that gas transport in the soil water phase can be neglected. This assumption is true for the most relevant gases (especially for ^{222}Rn, CO_2, CH_4), because the molecular diffusion coefficient of gases is 10^4 times smaller in water than in air and the solubility is of the order of 1 or even less.

4. ^{222}Rn concentration in soil air

Fig. 2 shows 3 ^{222}Rn concentration profiles from different sites down to a depth of 12 m (Fig. 2a) and 60 cm (Figs. 2b, c). The plotted curves are calculated from the theoretical steady state profile (eq. (4)). The profiles in Fig. 2a and 2b are satisfactorily reproduced using a relaxation depth of $\bar{z} = 170$ cm and $\bar{z} = 180$ cm and an equilibrium concentration $c_\infty = 390$ dpm l^{-1} and $c_\infty = 565$ dpm l^{-1}. The relaxation depth is in good agreement with the theoretical value of 138–185 cm and with experimental data from Hansen and Damkjaer (1987). The fraction f of ^{222}Rn that escapes from soil particles is estimated from the equilibrium ^{222}Rn concentration in soil air and the ^{226}Ra content of the soil material (cf. eq. (4c), $c_{Ra} = 1.8$ dpm g^{-1}, $\varepsilon = 0.2$, $\rho_b = 1.6$ g cm^{-3}) to be ~3% (profiles 2a and 2b), which is a typical value for sandy soils (Rama and Moore, 1984). ^{222}Rn profiles in Fig. 2 and profiles from other sites (Dörr and Münnich, 1987; Dörr et al., 1983) confirm the assumption of steady-state conditions, depth constant ^{222}Rn production and soil homogeneity (depth constant diffusion coefficient). Note that the depth scale in which ^{222}Rn

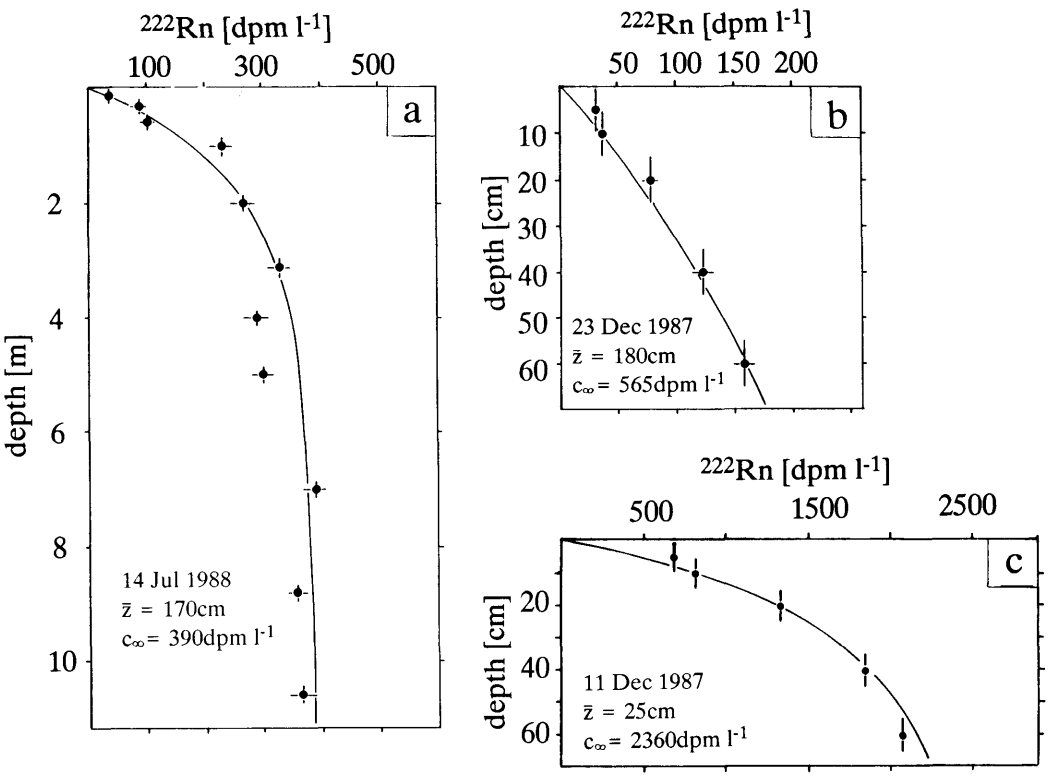

Fig. 2. ^{222}Rn concentration profiles in different soils and depth resolution. The curves are calculated from the theoretical steady state profile (eq. (40) using the parameters given in the figures. Profiles 2a and 2b are taken in a sandy forested soil, 15 km south of Heidelberg (Sandhausen); 2c is taken in a nearly water saturated clayey soil in the botanic garden of the Heidelberg University.

production and the diffusion coefficient are considered as constant is of the order of the relaxation depth ($\bar{z} \simeq 180$ cm).

Fig. 2c shows a ^{222}Rn profile in a clayey, almost water-saturated soil. This profile is also reproduced by the theoretical steady-state profile (eq. (4)) using a relaxation depth, however, of only $\bar{z} = 25$ cm and $c_\infty = 2360$ dpm l^{-1}. The short relaxation depth indicates that at high soil moisture content and, thus, at low available pore space, the diffusion resistance is not only due to variations of the diffusional cross section but also due to the smaller diffusion coefficient of ^{222}Rn in water ($D_{H_2O} \simeq 10^{-5}$ cm^2 s^{-1}) because gas transport through water-filled capillary regions (bottle necks) has to be considered at high soil moisture. The comparatively high equilibrium concentration of $c_\infty = 2360$ dpm l^{-1} is not due to an increased ^{222}Rn production at this site ($j_{Rn} = 4200$ dpm m^{-2} h^{-1}; $c_{Ra} = 2.8 \pm 0.4$ dpm g^{-1}), but also indicates the reduction of available pore space at high soil moisture content. Nevertheless, Fig. 2c shows that steady-state conditions and constant ^{222}Rn production can be assumed even at sites with extremely high soil moisture content.

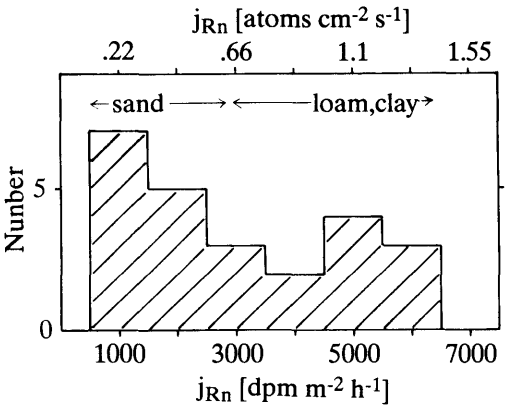

Fig. 3. Histogram of directly measured ^{222}Rn fluxes in West-Germany. The ^{222}Rn flux is given in dpm m^{-2} h^{-1} (lower abscissa) and atoms cm^{-2} s^{-1} (upper abscissa). The total number of investigated soils is $N_{tot} = 24$. The soils are roughly classified by their sand fraction (>62 μm). The soil is called "sandy" if the sand fraction >65% and "loamy, clayey" otherwise.

5. Direct ^{222}Rn flux measurements

5.1. *Spatial variation of the ^{222}Rn flux*

Fig. 3 shows a histogram of directly measured ^{222}Rn fluxes at 24 sites in West-Germany. 14 sites are located in an area of 50 km radius around Heidelberg. The other sampling locations are statistically distributed over North and South Germany. The samples are taken from cultivated fields and undisturbed forest soils. The ^{222}Rn flux varies between 500 and 6500 dpm m^{-2} h^{-1} in the restricted area around Heidelberg as well as in North and South Germany. A regional trend and significant differences between fluxes from cultivated and undisturbed soils are not observed. The average flux of 3200 dpm m^{-2} h^{-1} ($\Leftrightarrow$ 0.7 atoms cm^{-2} s^{-1}) and the flux variability are in good agreement with the global ^{222}Rn flux distribution (Turekian et al., 1977). The frequency distribution, however, suggests predominant ^{222}Rn fluxes of 1000–2000 dpm m^{-2} h^{-1} and 4000–6000 dpm m^{-2} h^{-1}. The wide range of the observed fluxes is supposedly due to the ^{222}Rn emanation rate, depending on the surface-to-volume ratio and, thus, on grain size diameter of soil particles. This is confirmed by the observation of lower ^{222}Rn fluxes (1000–2000 dpm m^{-2} h^{-1}) on sandy soils (>65% sand) and higher ^{222}Rn fluxes (4000–6000 dpm m^{-2} h^{-1}) on loamy and clayey soils (>35% clay), although the ^{226}Ra content is not significantly different in sandy soils (average; 2.2 ± 0.5 dpm g^{-1}) than in loamy and clayey soils (average: 3.2 ± 0.5 dpm g^{-1}).

5.2. *Temporal variation of the ^{222}Rn flux*

Fig. 4 shows a time series of direct flux measurements on a sandy soil (Fig. 4a) and on a clayey soil (Fig. 4b). The long-term average is 1030 ± 130 dpm m^{-2} h^{-1} and 4900 ± 1100 dpm m^{-2} h^{-1} (horizontal lines in Fig. 4a and b) at the sandy and clayey site, respectively. The ^{222}Rn flux from the sandy soil shows no significant seasonal variations, whereas at the clayey site, the ^{222}Rn flux tends to be higher in summer than in winter. The maximum deviation from the long-term average is $\pm 36\%$. This is supposedly due to the seasonal cycle of the soil moisture content. At higher soil moisture in winter, the tortuosity can increase due to an efficient blocking of bottle necks. This leads to a decrease of the relaxation depth and the ^{222}Rn flux at the soil surface (cf. eqs. (2), (4a) and (5)). Likewise,

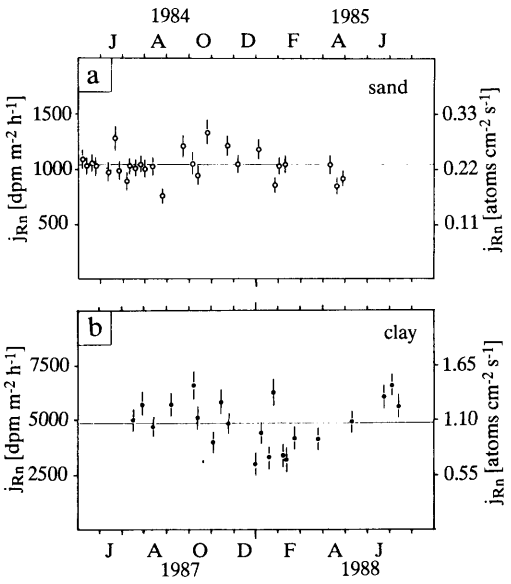

Fig. 4. Time series of direct ^{222}Rn flux measurements at a sandy site, 15 km south of Heidelberg (Sandhausen), between June 1984 and June 1985 (4a) and a clayey site, 12 km south west of Heidelberg (Nußloch), between July 1987 and July 1988 (4b). The long-term average (horizontal lines) at the sandy site is 1030 ± 130 dpm m^{-2} h^{-1}, and 4900 ± 1100 dpm m^{-2} h^{-1} at the clayey site.

the ^{222}Rn emanation rate and, thus the ^{222}Rn flux decreases at higher soil moisture content due to radioactive decay of ^{222}Rn during diffusion through soil water films. It is, however, difficult to quantify the influence of soil moisture on tortuosity and emanation rate because the diffusion resistance of the soil depends more on the abundance and distribution of very small soil pore diameters than on total soil moisture content. At a tortuosity increase from $k = 1.5$ to $k = 2.5$, the ^{222}Rn flux decreases by about 30%. In addition, radioactive decay in a water film of 2 cm total thickness decreases the apparent emanation rate by ~25%. This estimate shows that the observed ^{222}Rn flux variation at the clayey site (Fig. 4b) can be explained by a change of tortuosity and emanation rate due to seasonal variation of the soil moisture content. A reduction of the available pore space cannot cause a reduction of the steady state ^{222}Rn flux, because the decrease of soil permeability at increasing soil moisture content is compensated by the corresponding increase of soil air concentration (cf. eqs. (2) and (4c)).

The influence of temperature variations on the ^{222}Rn flux is estimated to be too small to be of practical importance in temperate climate regions. At a temperature change of 20°C and a penetration depth of the diurnal temperature cycle of ~10 cm, thermal expansion lifts the soil air column within the penetration depth by ~7 mm. Additional loss of ^{222}Rn from a 7 mm soil air layer increases the ^{222}Rn flux by ~0.4%. A similar estimate shows that the annual temperature cycle has also no influence on the ^{222}Rn flux. Average atmospheric pressure variations on a time scale of several days are of the order of ±1% (observations at the Institute's weather station). At a pressure drop of 1%, a soil air column of 10 m (corresponding to the depth of the groundwater table) is lifted by 10 cm, which leads to a ^{222}Rn flux increase by 6%. These are, however, only rough estimates of the influence of meteorological parameters on the ^{222}Rn flux in the region investigated, because restoration of natural steady state conditions by diffusion (time constant ≃ 5 days) is not considered. A detailed discussion of the effect of meteorological factors on the ^{222}Rn flux is given by Schery et al. (1984) and Clements and Wilkening (1975).

6. Permeability coefficient

The ^{222}Rn permeability coefficient, P_{Rn}, is defined by Ficks law no. 1 (eq. (1)) as the ratio of ^{222}Rn flux and concentration gradient. Fig. 5 shows the ^{222}Rn permeability, normalized to the molecular diffusion coefficient of ^{222}Rn in air, as a function of the available pore space. The ^{222}Rn permeability is calculated from simultaneous ^{222}Rn flux and concentration gradient measurements on various soils in West-Germany. The available pore space, ε, is calculated from measured total porosity, ε_0, and volumetric soil moisture content F ($\varepsilon = \varepsilon_0 - F$). Open circles indicate data from loamy and clayey soils; crosses represent measurements on sandy soils. The slope of the linear regression line is interpreted as the tortuosity (cf. eq. (2)). The abscissa offsets of 0.04 and 0.18, respectively, means that not the total pore space but only the "bottle necks" need to be

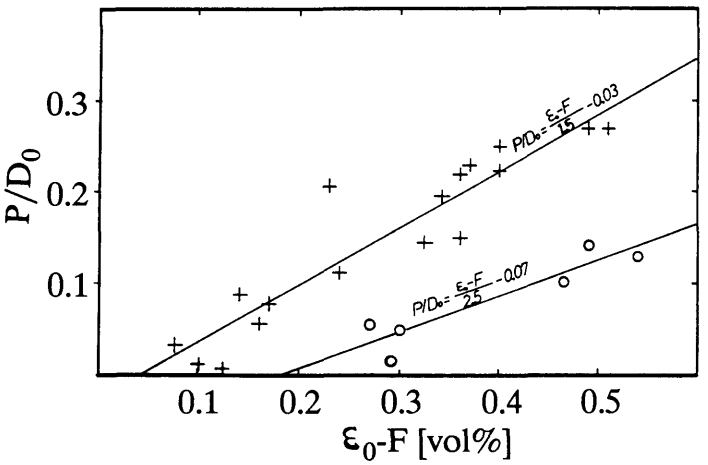

Fig. 5. Permeability (normalized to the molecular diffusion coefficient of ^{222}Rn in air) versus available pore space. The permeability is obtained from simultaneous ^{222}Rn flux and concentration gradient measurements. The available pore space is calculated from measured soil moisture and total porosity. Crosses indicate samples from sandy soils; open circles from loamy and clayey soils. The results of linear regression for both data sets are given in the figure.

filled with water to stop gaseous diffusion. The tortuosity of $k = 1.5$ and $k = 2.5$ for sandy and loamy/clayey soils, respectively, are in good agreement with data from Penman (1940) and Carman (1956), which are derived with classical hydrological methods.

The observed dependence of the normalized ^{222}Rn permeability on soil parameters allows calculation of the permeability of any other gas by replacing the molecular diffusion coefficient of ^{222}Rn in air by the molecular diffusion coefficient of the considered gas:

$$P_{gas} = P_{Rn} D_{0,gas}/D_{0,Rn}. \quad (11)$$

7. Determination of soil CO_2 and CH_4 fluxes

Fig. 6 shows a typical soil CO_2 and CH_4 profile taken at the same site. The corresponding ^{222}Rn profile is shown in Fig. 2b. Soil CO_2 concentration increases with depth due to microbial decomposition of soil organic material and root respiration. Methane is microbially decomposed and, thus, soil CH_4 concentration decreases with depth. The plotted curves show the theoretical steady-state profile calculated from eqs. (8a) and (8b). The CO_2 and CH_4 profiles show the same relaxation depth of 12 cm, indicating similar

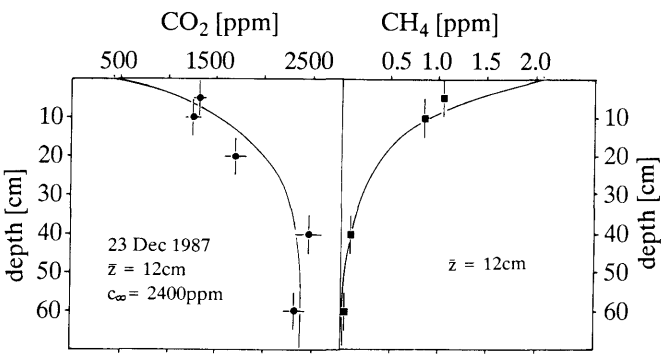

Fig. 6. Concentration profile of CO_2 and CH_4 in a sandy, forested soil (Sandhausen). The curves are calculated from the theoretical steady state profile (eqs. (8a) and (8b)) using the parameters given in the figure. The corresponding ^{222}Rn profile is shown in Fig. 2b.

depth distributions of the CO_2 source and the CH_4 sink. As an example, the CO_2 and CH_4 flux derived from the profiles in Fig. 6 and the permeability obtained from simultaneous ^{222}Rn flux and concentration profile measurements are compared with directly measured fluxes. The CO_2 and CH_4 fluxes are calculated from eqs. (10a) and (10b), using $j_{0,Rn} = 1970 \pm 160$ dpm $m^{-2} h^{-1}$ and the relaxation depth and equilibrium concentrations given in Figs. 2b and 6, to be $j_{CO_2} = 5.58 \pm 0.55$ mMol $m^{-2} h^{-1}$ and $j_{CH_4} = -(8.15 \pm 0.67)\ 10^{-3}$ mMol $m^{-2} h^{-1}$. The directly measured fluxes are $j_{CO_2} = 3.76 \pm 0.90$ mMol $m^{-2} h^{-1}$ and $j_{CH_4} = -(3.08 \pm 0.28)\ 10^{-3}$ mMol $m^{-2} h^{-1}$. The annual mean "^{222}Rn calibrated" CH_4 flux at this site is ~ 4 times higher than the average flux obtained from direct measurements. The CO_2 and CH_4 fluxes derived from concentration profile data and simultaneous ^{222}Rn flux measurements ("^{222}Rn calibrated fluxes") are, at all investigated sites, higher than directly measured fluxes. This is due to a reduction of the concentration gradient by the increasing CO_2 and decreasing CH_4 concentration under the inverted cup during measurements. If, however, the disturbance of the concentration gradient is minimized by short sampling times, small concentration changes with time lead to large errors in flux determination. The disturbance of the ^{222}Rn concentration gradient during flux measurement can practically be neglected due to the comparatively large relaxation depth ($\bar{z} \simeq 180$ cm) and high sensitivity of ^{222}Rn activity measurements (average ^{222}Rn activity under the inverted cup after ~ 1 h sampling time is only 1% of the equilibrium concentration). Moreover, direct CO_2 flux measurement can additionally be disturbed by CO_2 assimilation or respiration of above ground vegetation which is covered with the inverted cup. A discussion and comparison of directly measured and "^{222}Rn calibrated" CO_2 fluxes is given by Dörr and Münnich (1987)

Fig. 7 shows the methane concentration gradient at the soil surface (Fig. 7a) and the "^{222}Rn calibrated" CH_4 flux (Fig. 7b) at the same site between August 1987 and August 1988. Comparison of Figs. 7a and 7b indicates that flux determination from concentration profiles without knowledge of the actual permeability can result in a completely different time series than

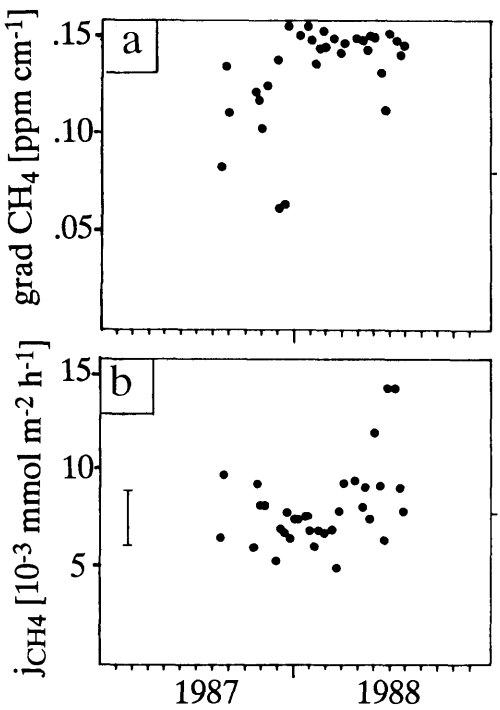

Fig. 7. Comparison of the CH_4 concentration gradient at the soil surface (Fig. 7a) and the "^{222}Rn calibrated" CH_4 flux (Fig. 7b) in a sandy, forested soil (Sandhausen) between August 1987 and July 1988.

"^{222}Rn calibrated" fluxes. The increase of the concentration gradient in December 1987, for example, is obviously due to a decreasing permeability and not caused by an increased CH_4 decomposition rate. The methane flux increase in June 1988 is supposedly due to an increasing permeability at a constant or even decreasing concentration gradient. The strong influence of the permeability on the methane flux in the soil indicates that microbial decomposition of CH_4 is primarily controlled by the transport of CH_4. For a detailed discussion of the soil CH_4 flux in aerated soils, see Born et al. (1990).

8. Conclusions

^{222}Rn proves to be a useful tracer for soil gas transport. Our measurements confirm the assumption of steady state conditions and depth

constant ^{222}Rn source strength. The spatial pattern of the ^{222}Rn flux is found to depend more on soil type than on the ^{226}Ra activity of the soil material. ^{222}Rn flux measurements at a sandy and clayey site during a period of 1 year show that a temporal varying ^{222}Rn flux is only expected on extremely wet soils due to seasonal varying soil moisture. The permeability coefficient P_{Rn}, obtained from simultaneous ^{222}Rn flux and concentration profile measurements in various soils, is expressed as a function of the soil parameters, namely, total porosity ε_0, soil moisture F, tortuosity k, and the molecular diffusion coefficient D_0 of ^{222}Rn in air: $P = D_0(\varepsilon_0 - F)/k - \text{const.})$. Our investigations show that regional mean ^{222}Rn fluxes can be determined sufficiently precisely to use atmospheric ^{222}Rn as tracer for vertical mixing and long-range air mass transport.

Determination of trace gas fluxes at the soil surface using ^{222}Rn as tracer for soil gas transport proves to give more reliable data than direct flux measurements by the inverted cup method. Soil gas fluxes obtained with the method described are independent of gas transport effects and, therefore, give information on soil gas production or decomposition rates.

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