INVESTIGATING GAS-WATER-ROCK CARBON ISOTOPE EXCHANGE IN THE FIELD

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ABSTRACT. Extensive investigations of isotope content and hydrochemical parameters in soil gas, soil material, groundwater and seepage water from a Quaternary aquifer show a good correlation between ^{14}C concentration of the groundwater and its mean residence time in the unsaturated zone. The initial ^{14}C concentration varies between 100 and 50% modern. It decreases through solution and dissolution of carbonates to 50% of the ^{14}C concentration of atmospheric CO_2.

INTRODUCTION

The carbon isotope concentration of groundwater samples from carbonatic aquifers with a short mean residence time (MRT), is mainly determined in the unsaturated zone. In very old groundwater, however, carbon isotope concentration of dissolved inorganic carbon (DIC) is mainly influenced by the carbon isotope concentration of rock carbonates.

To evaluate the initial ^{14}C concentration of groundwater (A_0), several hydrochemical correction models have been developed which, however, when applied to the same groundwater, differ greatly (eg, Fontes & Garnier, 1979; Eichinger, 1983). A_0 is the ^{14}C concentration of groundwater samples without radioactive decay.

From 1978 to 1987 detailed studies were carried out in the field to study the origin of the DIC in groundwater. We analyzed carbon and oxygen isotope concentrations of soil gas, rock material, seepage water and groundwater as well as organic matter.

FIELD STUDIES

The area of investigation was the Munich Gravel Plain, a Quaternary carbonate gravel aquifer, 1–10m thick. The mean groundwater flow velocities are in the range of 10–30m a day. The unsaturated zone overlying the groundwater surface is 10–50m thick. The Pleistocene carbonate gravels are covered with 30–50cm of soil; 90% of the gravel consists of calcite and dolomite; the remainder are sandstones and crystalline rock with interstitial lenses of sand and cemented gravel. There are study areas here, where gas samples can be taken from different depths down to groundwater and one field is used for sampling seepage waters. Core samples of soil were also collected.

[14]C/^{13}C DIC of Groundwater

The measured ^{14}C concentrations of our groundwater samples (^{14}C DIC) lie between 70 and 122% modern. MRTs were estimated from ^{3}H concentrations between 1 and 15 yr. Due to the similar hydrochemical compos-

ition of the groundwater samples, and their similar ^{13}C DIC concentrations from –14.5 to –12.2‰, a comparable initial ^{14}C concentration (A_0) would be expected for all groundwater samples. Since the ^{14}C concentration of atmospheric CO_2 increases with an increase in the MRT (Fig 1), the ^{14}C DIC is thus expected to increase, assuming comparable A_0 values. Figure 1 shows the contrary. The ^{14}C DIC decreases with an increase in the MRT. By comparing the ^{14}C concentration of atmospheric CO_2 with the ^{14}C DIC in groundwater (Fig 1), A_0 values of 50–100% of the atmospheric ^{14}C CO_2 concentration can be deduced.
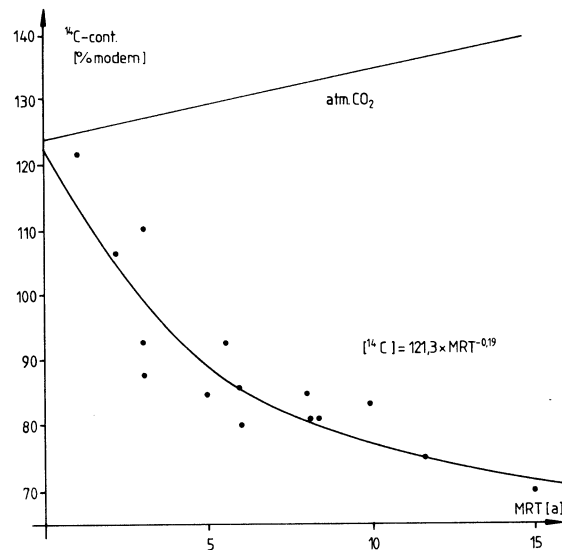

Fig 1. [14]C concentration of groundwater samples as a function of mean residence time (MRT) in comparison with the ^{14}C-concentration of atmospheric CO_2. Sampling time: 1984/85

[14]C CO_2 of Soil Gas

Figure 2 shows the ^{14}C depth profiles of soil gas CO_2 in two different fields. The "forest" profiles measured in 1979/80 and 1983–1985 show decreasing ^{14}C CO_2 concentration with increasing sampling depth. The differences between the two profiles can be explained by the decrease of the ^{14}C concentration in atmospheric CO_2.

The differences of the ^{14}C CO_2 concentration measured from 1983–1985 in the "forest" and "grass" areas, may be explained by different seepage velocities of water in the two fields. Measurements of the ^{3}H concentration of soil moisture in the forest site gave seepage velocities of 1.5–2m/a in contrast to the grass site, where 5–10m/a were obtained. Measurements of the [85]Kr concentration in soil gas gave "seepage velocities for gas" in the forest site of 2–3m/a (Eichinger *et al*, 1984). Transferring the results of the
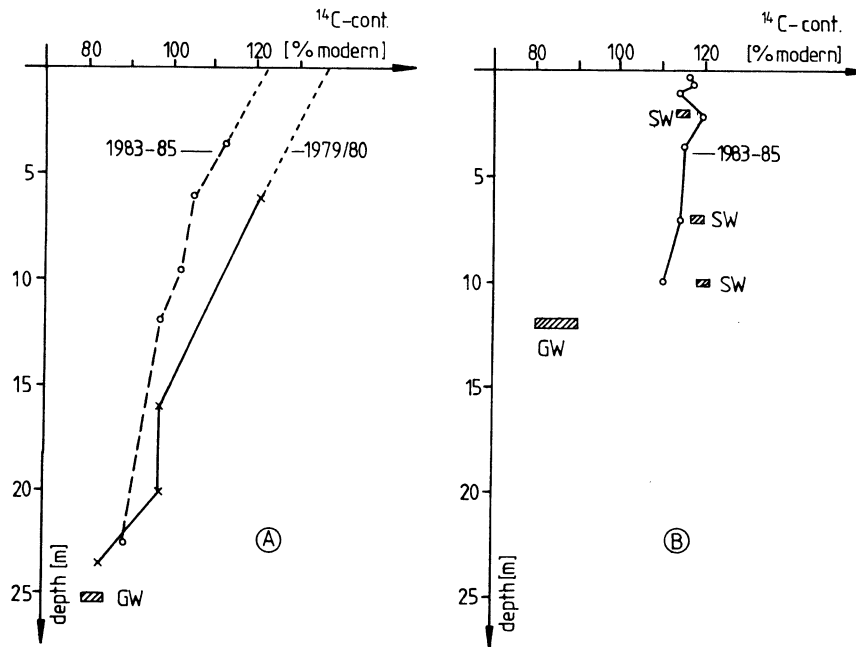
Fig 2. Averaged measured ^{14}C concentration of soil gas CO_2, seepage water (SW) and groundwater (GW). A. Forest study area. Study period: 1979/80, 1983–1985. B. Grass study area. Study period: 1983–1985.
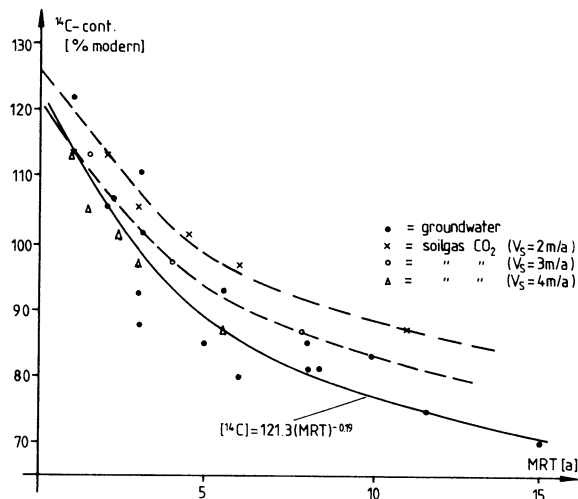

Fig 3. ^{14}C concentration of groundwater samples and soil gas CO_2 as a function of mean residence time (MRT). The soil gas samples are from different depths of the unsaturated zone. The MRT are calculated for various seepage velocities (V_s). The lines are calculated by exponential functions; dotted lines by the values of ($\times$) resp (o) and full line by ($\bullet$).

[14]C measurements in soil gas CO_2 (Fig 2) and of the MRT of the seepage water, as deduced from ^{3}H and [85]Kr measurements in relation to their sampling depths, we get the correlation shown in Figure 3 between seepage velocity and ^{14}C concentration of soil gas CO_2. A good correlation is seen, if a seepage velocity of 4m/a is assumed.

We can conclude from these results that the initial ^{14}C concentration of groundwater samples strongly depends on the mean residence time in the unsaturated zone.

Carbon Isotope Exchange

In the study areas calcite saturation of the seepage water is in a depth of 0.5 m. We can assume that the ^{14}C concentration of the soil gas CO_2 is in isotope equilibrium with the DIC of seepage water. The decrease in the ^{14}C concentration of soil gas CO_2 (Fig 2) is caused by processes of solution and precipitation of carbonates in the unsaturated zone (Hoppe *et al*, 1987). Variations of the CO_2 partial pressure, which were measured down to a depth of 23m, cause seepage waters to become oversaturated and under-saturated with respect to calcite. This is the reason for dilution of the ^{14}C in DIC.

The process of precipitation of carbonates should be measurable, by analyzing carbon and oxygen isotope concentrations on rock surfaces. Thus, we tried to dissolve chemically and mechanically the surfaces of rock and binding material. As can be seen from the measurements of ^{13}C and [18]O concentration, the results represent a mixing line (Fig 4). One endpoint represents the primary component ($\delta^{13}C = +1.0‰$; $\delta^{18}O = -4.0‰$) and the other the precipitated component. The ^{13}C and [18]O concentration of this com-
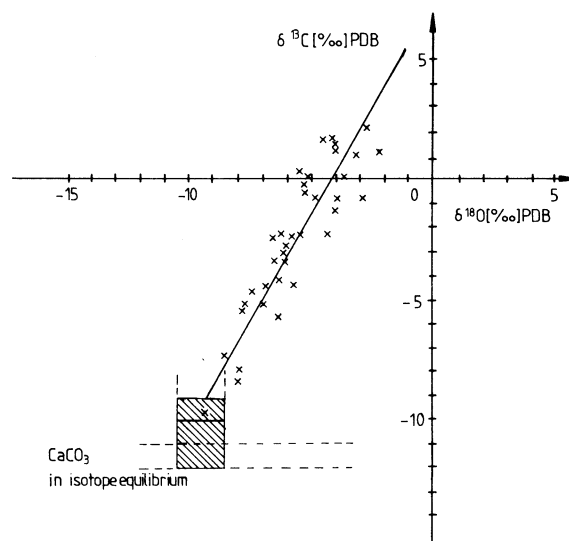

Fig 4. [13]C and [18]O concentrations of carbonates. The hatched area marks the $\delta^{13}C$ and $\delta^{18}O$ values of carbonates precipitating under equilibrium with the seepage water respectively under kinetic fractionation.

ponent can be deduced from the results of isotope analyses of seepage water and are near -10 $\delta^{13}C$-‰ and -10 $\delta^{18}O$-‰.

Samples of cemented gravel from boreholes at the forest site were prepared for measuring ^{14}C concentration in a special preparation line. Weak acid was added at a rate of 10ml/day to the rock material in a closed system. The reaction vessel was filled with 10L of distilled water and ca 5kg of sample. The CO_2 produced was flushed with N_2 as carrier gas. In 3 of 6 samples, ^{14}C could be detected.

From the measurements of the ^{14}C concentration of soil gas CO_2, of the mean DIC concentration of seepage water (5.5mmol/L) and of the CO_2 concentration (0.5 vol–%) of soil gas as well as the water content (4.5 vol–%) and the porosity (30 vol–%), the amount of carbon can be estimated, which precipitates out from DIC in the forest site between depths of 6 – 22m. The precipitation rate of carbonate is near 30g $CaCO_3/m^2a$ at a seepage velocity of 2m/a and 15g $CaCO_3/m^2a$ at a velocity of 4m/a. Thus, assuming boundary conditions for the last 10,000 yr were similar to those of today, only 0.5 – 2 mass–% of the total amount of carbonate has been precipitated from seepage water.

Open and Closed System

^{13}C concentrations of soil gas CO_2, seepage water, and groundwater show that, with respect to the gaseous phase in each level of the unsaturated zone, the system is open (Eichinger, 1987). Measurements of the ^{14}C concentrations show that, in the unsaturated zone, almost no CO_2 exchange occurs between the soil zone and deeper layers of the unsaturated zone.

CONCLUSION

In carbonate aquifers of the type investigated, the initial ^{14}C concentration of groundwater samples is a function of the mean residence time of the seepage water in the unsaturated zone. The measured decrease of ^{14}C concentration in young groundwater, in comparison to the ^{14}C CO_2 concentration in the soil zone, is due to carbon isotope exchange between soil gas CO_2, DIC and rock carbonate. The exchange is caused by carbonate solution and precipitation processes.

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REFERENCES

Eichinger, L, 1983, A contribution to the interpretation of ^{14}C groundwater ages considering the example of a partially confined sandstone aquifer, *in* Stuiver, M and Kra, RS, eds, Internatl ^{14}C conf, 12th, Proc: Radiocarbon, v 25, no. 2A, p 347–356.
————— 1987, Isotopic and geochemical studies investigating the genesis of carbon isotope content in young groundwaters, *in* Isotope techniques in water resources development, Proc: Vienna, IAEA, p 89–100.

Eichinger, L, Salvamoser, J, Stichler, W, Merkel, B and Nemeth, G, 1984, Seepage velocity
    determination in unsaturated quaternary gravel, *in* Udluff, P, Merkel, B and Proesl, K H,
    eds, Recent investigation in the zone of aeration, Internatl symposium, Recent investiga-
    tions in the zone of aeration, Proc: Tech Univ Munich, v 1, p 303–313.
Fontes, J C and Garnier, J M, 1979, Determination of the initial ^{14}C activity of the total dis-
    solved carbon: a review of the existing models and a new approach: Water Research, v 15,
    p 399–413.
Hoope, J, Merkel, B, Eichinger, L and Hofmann, M, 1987, Nachweis von Carbonatausfällung
    im Boden mit Hilfe von Isotopenuntersuchungen: Zeitschr Wasser-Abwasser-Forsch, v 20,
    p 16–21.