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δ^{13}C pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges mountains, France)

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Abstract

The transfers and origins of dissolved inorganic carbon (DIC) were studied for a year in a soil–spring–stream system in the Strengbach catchment, Vosges mountains, France. This 80 ha experimental research basin is located on the eastern side of the mountains, at an altitude ranging from 883 to 1146 m.a.s.l. and is mainly covered by spruce (80%). Brown acid and podzolic soils developed on a granitic basement, and, as a result, the DIC originates solely from CO_2 generated by oxidation of soil organic matter. The ($\delta^{13}C_{DIC}$) in catchment waters is highly variable, from about −22‰ in the springs and piezometers to about −12‰ in the stream at the outlet of the catchment. In the springs, pronounced seasonal variations of $\delta^{13}C_{DIC}$ exist, with the DIC in isotopic equilibrium with the soil CO_2 that has estimated δ^{13}C of about −24‰ in winter and −20‰ in summer. These seasonal variations reflect an isotopic fractionation that seems only induced by molecular diffusion of soil CO_2 in summer. In stream water, seasonal variations are small and the relatively heavy DIC (−12‰ on average) is a result of isotopic equilibration of the aqueous CO_2 with atmospheric CO_2.

Keywords: δ^{13}C; Dissolved inorganic carbon; Strengbach case study

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1. Introduction

The dissolved inorganic carbon (DIC) in river water has three main sources: soil CO_2, dissolution of carbonate minerals and atmospheric CO_2 exchanged trough the air–water interface (Yang et al., 1996). On average, the contribution of soil CO_2 to the DIC in the world rivers has been estimated to be about 67% (Berner et al., 1983; Meybeck, 1987; Amiotte Suchet and Probst, 1995; Ludwig et al., 1997). In each river, the respective contribution of soil CO_2 and of carbonate mineral dissolution can only be estimated using modeling approaches (Probst, 1992; Amiotte Suchet and Probst, 1993a,b; Probst et al., 1994a,b; Amiotte Suchet and Probst, 1995; Lud-

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wig et al., 1997). On the other hand, many studies have measured the stable carbon isotope composition of the DIC, attempting to distinguish its sources in river water (Hitchon and Krouse, 1972; Mook and Tan, 1991; Tan and Edmond, 1993; Pawellek and Veizer, 1994; Cameron et al., 1995; Yang et al., 1996). Yet, despite the fact that carbon isotopic signatures of carbonate minerals and of soil CO_2 are distinctive, the variations of carbon isotope composition of riverine DIC remain quite difficult to interpret, because additional processes, such as riverine respiration and isotopic equilibration with atmospheric CO_2 play a role.

Clearly, a better knowledge of the processes that affect the isotopic composition of the DIC in the upstream parts of the river basins is needed (Pawellek and Veizer, 1994). To our knowledge, only two studies have focused as yet on isotopic composition of DIC in small watersheds: the work of Dandurand et al. (1982), for a stream draining carbonate rocks, and Kendall et al. (1992, 1995) for two streams draining predominantly silicate rocks.

In this work, we have studied the stable isotopic composition of DIC in the springs and streams of a small watershed that drains a strictly silicate basement, which means that DIC originates solely from soil CO_2. Its spatial and temporal variations during a complete hydrological cycle enable us to quantify the role of soil and atmospheric CO_2 on the isotopic composition of DIC in a small homogeneous aquatic system.

2. Materials and methods

2.1. $\delta^{13}C$ of dissolved inorganic carbon (DIC) in terrestrial aquatic systems

2.1.1. Dissolved inorganic carbon (DIC)

The DIC is composed of aqueous carbon dioxide ($CO_2(aq)$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. These aqueous compounds can be in contact with gaseous carbon dioxide (CO_2 (g)) and/or carbonate minerals such as calcite ($CaCO_3$). The composition of DIC in continental water is then controlled by the chemical equilibria among these five species and is characterized at 25°C by the following equilibrium constants (Bourrié, 1976):

$$K_H = ([H_2CO_3^*]/pCO_2) = 10^{-1.46} \quad (1)$$

$$K_1 = ([H^+][HCO_3^-])/[H_2CO_3^*] = 10^{-6.35} \quad (2)$$

$$K_2 = ([CO_3^{2-}][H^+])/[HCO_3^-] = 10^{-10.33} \quad (3)$$

$$K_C = [Ca^{2+}][CO_3^{2-}] = 10^{-8.47} \quad (4)$$

Note that in Eq. (1), $H_2CO_3^*$ is the analytical sum of aqueous CO_2 (CO_2aq) and of the true carbonic acid (H_2CO_3). It is generally assumed that the concentration of aqueous CO_2 is nearly identical to $H_2CO_3^*$ (Stumm and Morgan, 1981).

The concentration of each species in solution therefore depends on its pH, partial pressure of CO_2 (pCO_2) and temperature. In stream water, DIC is mainly composed of HCO_3^- ions, while in soil solutions, with usually high pCO_2 and low pH values, DIC is mainly composed of $H_2CO_3^*$.

In small watersheds, HCO_3^- ions can have two distinct origins: the soil CO_2 and carbonate mineral dissolution. Three alternatives can be considered for the origin of DIC.

For silicate weathering by carbonic acid, such as albite hydrolysis (see Eq. (5)), DIC originates solely from soil CO_2.

$$\underset{\text{albite}}{\underline{2NaAlSi_3O_8}} + \underset{\text{soil } CO_2}{\underline{2CO_2 + 3H_2O}} \rightleftarrows \underset{\text{kaolinite}}{\underline{Al_2Si_2O_5(OH)_4}} + \underset{\text{solute compounds}}{\underline{2Na^+ + 2HCO_3^- + 4SiO_2}} \quad (5)$$

For carbonate dissolution by carbonic acid (Eq. (6)), one-half of the DIC originates from the mineral itself and the other half from the soil CO_2.

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \quad (6)$$

For carbonate dissolution by acids other than H_2CO_3 (e.g., sulfuric or organic acids), DIC originates solely from carbonate minerals (Eq. (7)).

$$2CaCO_3 + H_2SO_4 \rightleftarrows Ca^{2+} + 2HCO_3^- + SO_4^{2-} \quad (7)$$

The two first processes are believed to predominate in rock weathering (Garrels and Mackenzie, 1971; Wollast and Mackenzie, 1983; Meybeck, 1987; Amiotte Suchet, 1995) and, at the global scale, about two-thirds of bicarbonate ions transported by the world rivers originates therefore from soil CO_2.

2.1.2. Isotopic composition ($\delta^{13}C$) of soil CO_2

In the case of silicate rock weathering (Eq. (5)), the isotopic composition of DIC should reflect that of soil CO_2 that is produced by decomposition of soil organic matter (SOM) and by root respiration. Several processes lead the isotopic composition of soil CO_2 to be slightly different from that of SOM.

The $\delta^{13}C$ of SOM is directly related to the type of vegetation cover with an estimated average of −26‰ (−22 to −30‰) for C3 plants and −12‰ for C4 plants (Deines, 1980; Mariotti, 1991). This original isotopic signature of SOM is slightly enriched in ^{13}C (about 1 to 4‰) during its mineralization. As a result, the $\delta^{13}C$ of SOM is progressively heavier with increasing depth and decreasing carbon content (Mariotti, 1991; Peterschmitt, 1991; Desjardins et al., 1991, 1994).

In addition, fractionation also occurs during the decay of SOM (Rightmire and Hanshaw, 1973; Dörr and Münnich, 1980; Salomons and Mook, 1986; Cerling et al., 1991), leading to an enrichment in ^{13}C of the residual soil CO_2. This is due to the molecular diffusion of the gas through the soil pores (Craig, 1954; Dörr and Münnich, 1980; Cerling et al., 1991). Depending on the study, the enrichment ranges from 1 to 4‰, with a maximum 4.4‰ claimed by Cerling et al. (1991). Then, taking into account a $\delta^{13}C$ value for SOM of −25‰, the maximum $\delta^{13}C$ of soil CO_2 can be estimated to about −21‰.

Alternatively, soil CO_2 can sometimes originates from a mixture of atmospheric and soil air (Galimov, 1966; Rightmire, 1978; Cerling, 1984; Salomons and Mook, 1986; Cerling et al., 1991), as indicated by a negative relationship between the $\delta^{13}C$ of soil CO_2 and its associated partial pressures (pCO_2), for several soils in temperate climate and covered by C3 plants. In summer, the rate of SOM oxidation is high, inducing high pCO_2 in soils and preventing atmospheric CO_2 from penetrating the soil. As a result, the $\delta^{13}C$ of soil CO_2 is low, close to that of SOM. In contrast, the soil biologic activity is low in winter, permitting atmospheric CO_2 ($\delta^{13}C$ of about −8‰) to penetrate the soil, leading to an enrichment in ^{13}C. As a consequence, the $\delta^{13}C$ of soil CO_2 ranges between −20 and −26‰ in summer (Rightmire, 1978; Dörr and Münnich, 1980) and between −10 and −15‰ in winter (Cerling et al., 1991).

2.1.3. Isotopic fractionation between DIC and gaseous CO_2

The isotopic fractionation factors between the different carbonate species dissolved in continental water and gaseous CO_2 are now well known (Vogel et al., 1970; Deines et al., 1974; Mook et al., 1974; Wigley et al., 1978; Faure, 1986; Zhang et al., 1994; Szaran, 1998). In earth surface environments, fractionation is a linear function of temperature. The relationships between the isotopic enrichment factors (ε) and the temperature (T) are shown in Table 1.

Potential variations of carbon isotopic composition ($\delta^{13}C$) in an aqueous system are shown in Fig. 1. For DIC originating solely from soil CO_2, HCO_3^- ions should be enriched in ^{13}C by about 8 to 10‰ (Table 1), whereas the aqueous CO_2 should be depleted by about 1‰. In contrast, HCO_3^- ions from dissolution of carbonate rocks should not show any fractionation relative to precursor carbonate minerals. If so, for catchments covered by C3 plants ($\delta^{13}C = -26‰$), with no contamination of the soil CO_2 by atmospheric CO_2 and laying on non-carbonate rocks, the isotopic composition of DIC in

Table 1

Isotopic enrichment factors (ε) between gaseous CO_2, and dissolved carbonate species ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) as a function of temperature (in °C) (from Zhang et al., 1994)

Relationships between isotopic enrichment factors (ε, in ‰) and temperature (T, in °C)		ε in ‰	
		at 5°C	at 25°C
$\varepsilon CO_2 g(H_2CO_3^*) = (0.0049 \times T) - 1.31$	(8)	−1.29	−1.19
$\varepsilon CO_2 g(HCO_3^-) = (-0.1141 \times T) + 10.78$	(9)	+10.21	+7.93
$\varepsilon CO_2 g(CO_3^{2-}) = (-0.052 \times T) + 7.22$	(10)	+6.96	+5.92

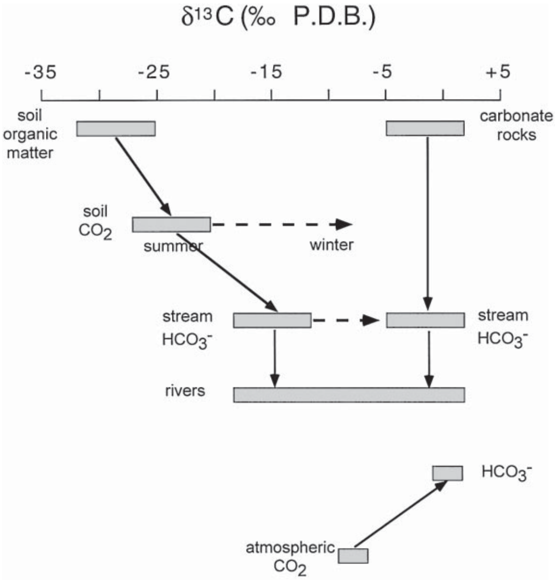


Fig. 1. Potential variations of carbon isotopic composition in aqueous systems (modified from Pawellek and Veizer, 1994).

stream water, mainly HCO_3^- ions, should vary between −16 to −19‰.

Finally, if the DIC is completely in isotopic equilibrium with atmospheric CO_2, its isotopic signature should vary between 0 and +2‰ (Fig. 1).

2.2. Site location

The isotopic composition of DIC in spring and stream water has been studied during one year in the Strengbach basin (Fig. 2).

The forested Strengbach catchment is located on the eastern side of the Vosges mountains (northeastern France), 58 km southwest from Strasbourg. It ranges from 883 m at the outlet to 1146 m at the top (Fig. 2). This small catchment (80 ha) lies mainly on a base poor leucogranite (the 320 My old Brézouard granite). At the top edge of the basin, a banded gneiss lies in contact with this granite (Probst et al., 1992). The fresh bedrock is overlaid with 1–10 m of saprolite. Despite the fact that the Brézouard leucogranite is somewhat affected by hydrothermal activity, no hydrothermal carbonate minerals, such as calcite, have been observed (El Gh'mari, 1995). We therefore consider all the DIC in the water of the Strengbach catchment to be derived from soil CO_2.

Brown acid soils are developed on the south facing slope, while podzolic soils cover the north facing slope. The valley bottom is occupied by a saturated area with hydromorphic soils, accounting for 2% of the catchment area. The soils are 0.8–1 m thick.

The vegetation cover is composed of C3 plants. Norway spruce (*Picea abies* L.) dominates (80% of the catchment area), and mixed silver fir (*Abies alba* L.) and beech (*Fagus sylvatica* L.) cover the rest of the area.

The Strengbach catchment has been monitored since late 1985, within the framework of the influence of acid precipitation on surface water chemistry and weathering (Probst et al., 1987, 1990a, 1992, 1994a,b, 1995). The chemistry of the stream water (Probst et al., 1992) is dominated by SO_4^{2-} and Ca^{2+} and the alkalinity is quite low ($pH = 6.10$ and $alk = 36.0\ \mu eq\ l^{-1}$, on average, for the year 1994–1995).

2.3. Sampling and analytical methods

2.3.1. Soil organic matter sampling

Four representative soil profiles (two acid brown soils under Norway spruce (*P. abies* L.) and beech (*F. sylvatica* L.)), one podzolic soil (under Norway spruce) and the hydromorphic soil of the saturated area have been sampled every 10 cm, down to the bedrock.

2.3.2. Water sampling

The location of each sampling point is presented in Fig. 2. The main stream has been sampled every week at the outlet gauging station (RS) of the Strengbach catchment, from November 1994 to December 1995. During this period, the surface water from 17 other sites has been sampled 5 times. Of these sampling sites, three are located on the main stream (upstream point R1, upstream of the saturated area RAZS and the outlet the gauging station RS), four are located on secondary streams (R3, BH, RH, RUZS), six correspond to springs (CS1, CS2, CS3, CS4, SH, SG) and four are piezometers of the saturated area (PA, PD, PF, PH).

The samples were filtered in the field through a 0.45 μm Millipore membrane, applying a small underpressure with a hand-operated vacuum pump. The

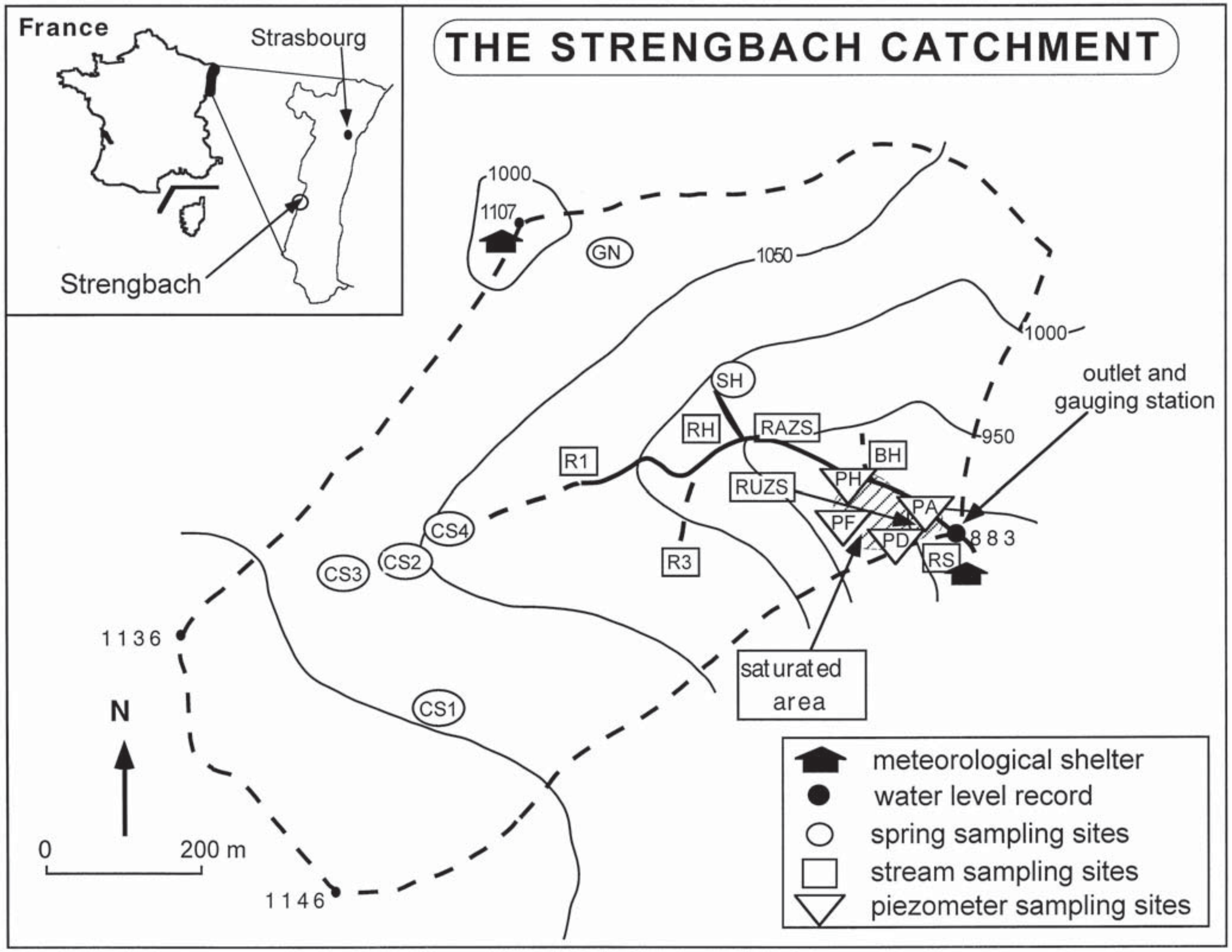


Fig. 2. Location and description of the Strengbach catchment.

membrane was pre-washed with 500 ml of deionized water. The samples for major element analysis were collected in 250 ml polyethylene bottles and those for isotopic analysis of DIC in 500 ml polyethylene bottles, poisoned with 1 ppm of $HgCl_2$ to prevent any microbial activity. Bottles were carefully sealed, taking care that no trapped air remained in contact with the sample. Finally, samples were kept between 0 and +5°C prior to analysis.

The $\delta^{13}C_{DIC}$ was measured at the Centre de Géochimie de la Surface, in Strasbourg, following the procedure of Kroopnick et al. (1970). Phosphoric acid (H_3PO_4) is added to the sample inside a vacuum line and the evolved CO_2 is purified and trapped with liquid nitrogen in a glass tube. The isotopic composition of this gaseous CO_2 was then measured with a VG Optima mass spectrometer. Several tests have been made for low alkalinity water, including the filtering step in the field. The resulting analytical precision was ±0.2‰. The major elements (calcium, magnesium, potassium and sodium) were determined by Atomic Absorption Spectrophotometry, chloride, sulfate, nitrate by Liquid Ion Chromatography and alkalinity by titration with the Gran method.

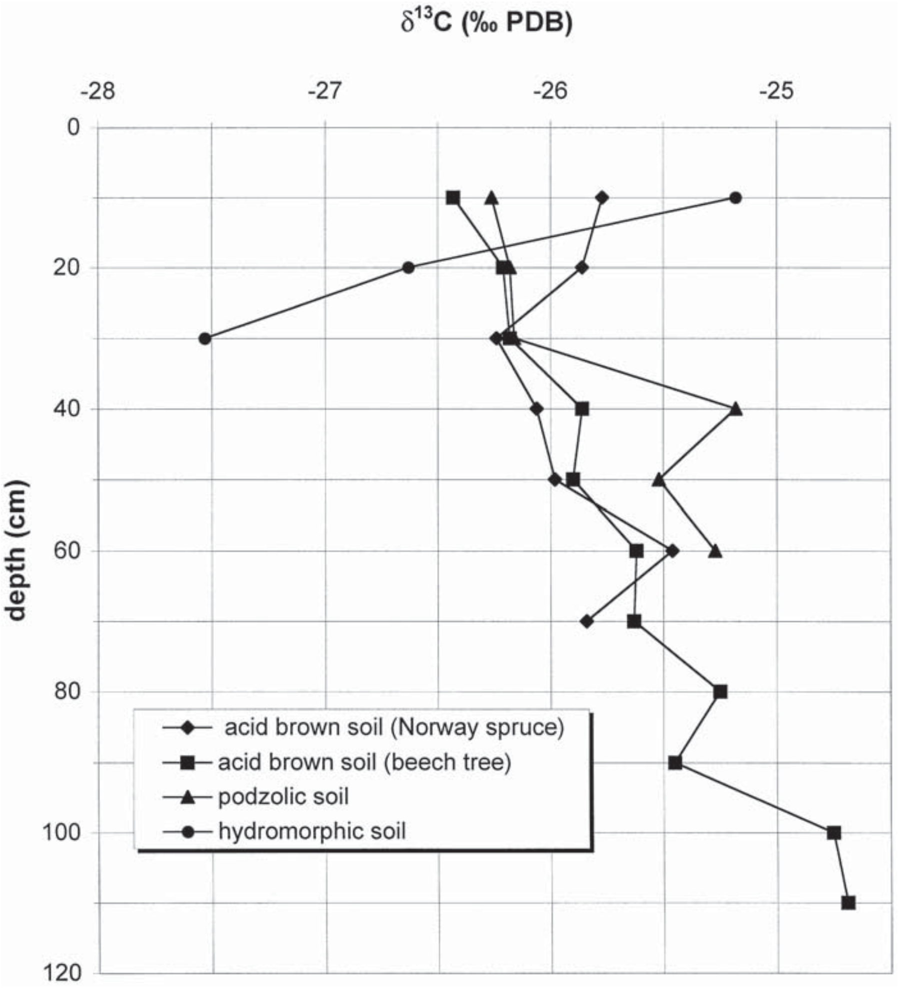


Fig. 3. Variation of $\delta^{13}C$ for the soil organic matter in the different soil profiles of the Strengbach catchment.

3. Results

3.1. $\delta^{13}C$ values of soil organic matter

In the Strengbach catchment, the isotopic composition of SOM, the primary source of the DIC in the stream water, is typical of C3 plant covers, with $\delta^{13}C$ of −24.7 to −26.4‰ for the acid brown and the podzolic soils and a small enrichment in ^{13}C with increasing depth (Fig. 3). This ^{13}C enrichment correlates with the decrease of carbon content (Fig. 4). These results are similar to those of Balesdent and Mariotti (1996) for French soils, and typical of other soils in equilibrium with C3 plants (Andreux et al., 1990; Desjardins et al., 1991, 1994; Koutika et al., 1997 among others). This depth pattern can be interpreted as an isotopic fractionation of SOM by decomposing organisms, with the young and labile fraction (the easily mineralized SOM) depleted in ^{13}C relative to the residual SOM (Boutton, 1996). Note, however, that the hydromorphic soil of the saturated area shows different patterns. In the first 10 cm of the profile, the organic carbon is quite heavy ($\delta^{13}C = -25.2‰$), becoming lighter with increasing depth (Fig. 3). This surprising pattern can perhaps be explained by the degradation of SOM under anaerobic conditions. As reported by Wada and Ueda (1996) from a rice paddy field in Japan, aerobic bacterial

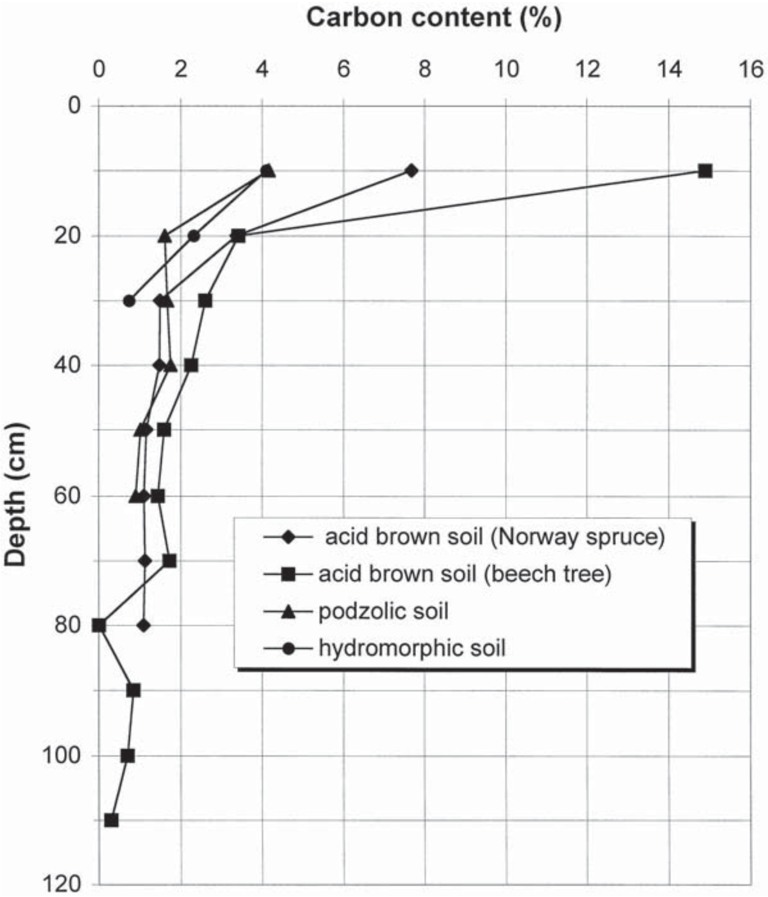


Fig. 4. Variation of carbon content of the soil organic matter in the different soil profiles of the Strengbach catchment.

decomposition of SOM produces very depleted methane (δ^{13}C around −50‰) but relatively enriched CO_2 (δ^{13}C from −9 to −12‰). Such processes lead to a decrease in the δ^{13}C of the accumulated SOM (−29.2‰) relative to the fresh organic matter (−26.8‰). Additional studies are required in order to establish to what extent the soil CO_2 could be isotopically contaminated by CH_4.

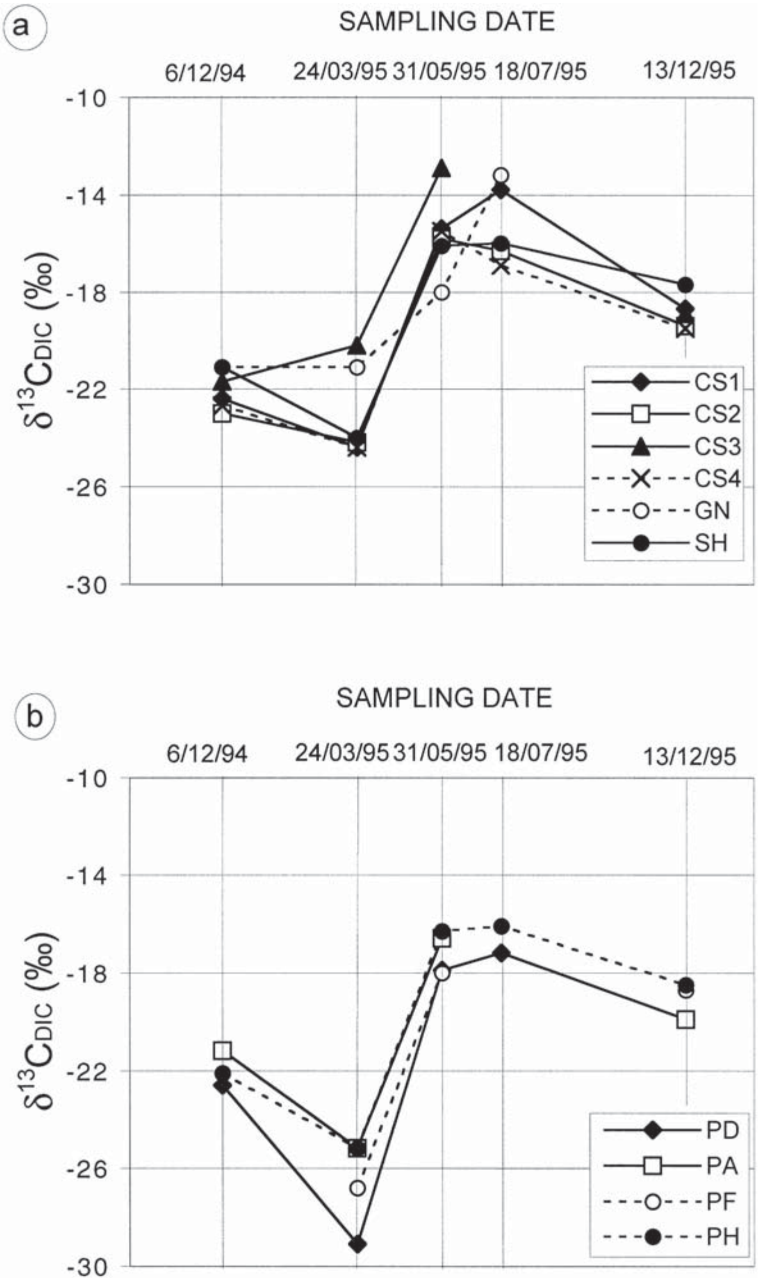


Fig. 5. Temporal fluctuations of $\delta^{13}C_{DIC}$ in the springs (CS1, CS2, CS3, CS4, GN, SH) and the piezometers (PA, PD, PF, PH) of the Strengbach catchment (see Fig. 2 for location of sampling sites).

Assuming an isotopic enrichment of +1 to +4‰ induced by molecular diffusion of CO_2 in soil pores (see above), the $\delta^{13}C$ of the soil CO_2 produced by SOM mineralization in the Strengbach catchment should range between −25 and −21‰ (between −26.5 and −21.5‰ for the hydromorphic soil of the saturated area).

3.2. $\delta^{13}C$ of DIC in spring water and piezometer

The variations of the isotopic composition of the DIC in spring water and in the piezometers of the saturated area are represented in Fig. 5. On average, the $\delta^{13}C_{DIC}$ is quite low, with mean values of −18.9 and −20.3‰ for spring water and piezometers, respectively (Table 2). This is the result of higher concentrations of $H_2CO_3^*$, isotopically equilibrated with light soil CO_2, relative to HCO_3^- ions. Nevertheless, the $\delta^{13}C_{DIC}$ values shows significant, station independent, seasonal variations (Fig. 5). In winter 1994/95, the $\delta^{13}C_{DIC}$ values vary on average between −26.6 and −23.2‰, that is in the estimated range of the soil CO_2. Subsequently, in the late spring and in summer, DIC becomes enriched in ^{13}C, with mean values ranging between −16.7 and −15.1‰. The following 1995 winter, shows return to more negative values (−19.3‰ on average), but not a recover to the values of December, 1994.

Note also that the $\delta^{13}C_{DIC}$ values in piezometers are generally more depleted than those of the spring water (Table 2). This perhaps can be related to the isotopic composition of the soil organic matter and soil gases in the saturated area, considering that the proportions of DIC species ($H_2CO_3^*$ vs. HCO_3^-), are similar in spring and in piezometers. Whatever the explanation, the enrichment in ^{13}C (about 7–8‰) between winter and summer samples, is also recorded in piezometers as well.

3.3. $\delta^{13}C$ values of DIC in stream water

DIC in stream water is clearly enriched in ^{13}C (Fig. 6) with a yearly average of −11.8‰. Note however that, in contrast to springs and piezometers, no clear seasonal variations are indicated. In general, the $\delta^{13}C_{DIC}$ ranges between −13.8‰ and −9.3‰

Table 2
Average values and ranges of $\delta^{13}C_{DIC}$, HCO_3^- concentrations and pCO_2 in springs and piezometers for 5 sampling campaigns

Sampling date	Number of sample			$\delta^{13}C_{DIC}$		HCO_3^- (meq l^{-1})		log pCO_2 (atm.)	
	Piezo	Springs		Pz	Sp	Pz	Sp	Pz	Sp
6/12/94	3	6	Mean	−22.0	−22.0	0.050	0.062	−2.92	−3.01
			Min	−22.6	−23.0	0.009	0.022	−3.15	−3.11
			Max	−21.2	−21.1	0.098	0.131	−2.79	−2.89
24/03/95	4	6	Mean	−26.6	−23.2	0.052	0.033	−2.22	−2.41
			Min	−29.1	−24.4	0.010	0.006	−2.62	−2.71
			Max	−25.2	−20.2	0.102	0.080	−1.79	−2.18
31/05/95	4	4	Mean	−17.2	−15.6	0.063	0.055	−2.85	−3.00
			Min	−18.0	−18.0	0.021	0.043	−3.29	−3.06
			Max	−16.3	−12.9	0.119	0.086	−2.58	−2.91
18/07/95	2	5	Mean	−16.7	−15.1	0.114	0.052	−2.97	−2.99
			Min	−17.2	−16.9	0.109	0.016	−3.01	−3.17
			Max	−16.1	−13.2	0.119	0.114	−2.92	−2.86
13/12/95	4	5	Mean	−19.3	−18.8	0.030	0.034	−3.13	−3.16
			Min	−19.9	−19.5	0.000	0.005	−3.29	−3.60
			Max	−18.5	−17.7	0.083	0.049	−2.97	−2.99
Total	17	26	Mean	−20.3	−18.9	0.062	0.047	−2.82	−2.91
			Min	−29.1	−24.4	0.000	0.005	−3.29	−3.60
			Max	−16.1	−12.9	0.119	0.131	−1.79	−2.18

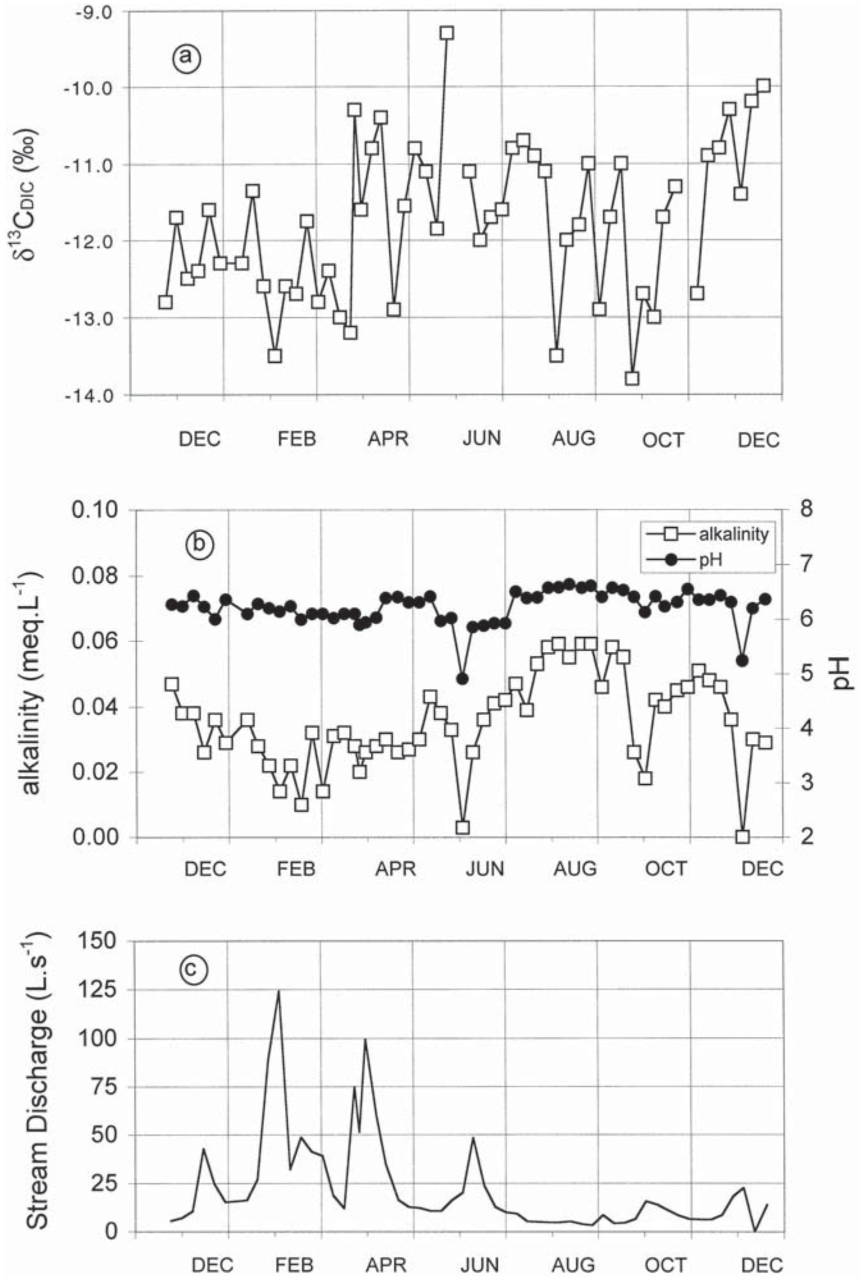


Fig. 6. Weekly fluctuations (22/11/94 to 13/12/95) of (a) $\delta^{13}C_{DIC}$, (b) alkalinity and pH and (c) stream discharge in the Strengbach stream at the outlet from the catchment (site RS).

and, although it tends to be more depleted in winter than in the spring and summer, the trend is not significant. For the upper part of the main stream and for secondary stream water, more depleted $\delta^{13}C_{DIC}$ values have been observed (up to −19.6‰). This overall downstream enrichment in ^{13}C is evident across the entire catchment (Table 3). The most depleted $\delta^{13}C_{DIC}$ values were recorded in the stream

Table 3
Average values and ranges of $\delta^{13}C_{DIC}$, HCO_3^- concentrations, pCO_2 and pH in stream water for each sampling site, as calculated from the measurements of the 5 sampling campaigns (sampling sites are listed in increasing order of the estimated distances from springs)

Sampling site		$\delta^{13}C_{DIC}$ (‰ PDB)	HCO_3^- (meq l^{-1})	log pCO_2 (atm.)	pH
R3	Mean	−17.3	0.000	n.c.	5.00
	Min	−18.5	0.000	n.c.	4.89
	Max	−16.6	0.000	n.c.	5.25
RUZS	Mean	−17.2	0.019	−2.79	5.83
	Min	−19.6	0.000	−2.91	5.63
	Max	−15.8	0.049	−2.73	6.24
BH	Mean	−10.6	0.092	−2.86	6.58
	Min	−12.4	0.058	−2.95	6.27
	Max	−9.3	0.114	−2.69	6.79
R1	Mean	−15.9	0.025	−2.86	6.01
	Min	−17.3	0.015	−2.93	5.81
	Max	−14.4	0.035	−2.82	6.19
RH	Mean	−13.4	0.042	−2.90	6.23
	Min	−15.6	0.018	−3.04	5.84
	Max	−11.4	0.058	−2.77	6.62
RAZS	Mean	−11.7	0.026	−2.99	6.17
	Min	−13.3	0.016	−3.09	5.92
	Max	−10.7	0.035	−2.90	6.38
RS	Mean	−10.9	0.035	−2.94	6.21
	Min	−12.5	0.020	−3.09	5.90
	Max	−10.0	0.053	−2.78	6.44

draining the upper horizons of the saturated area (RUZS), which is consistent with measurements in the piezometers of the same area.

4. Factors controlling the δ^{13}C values of DIC

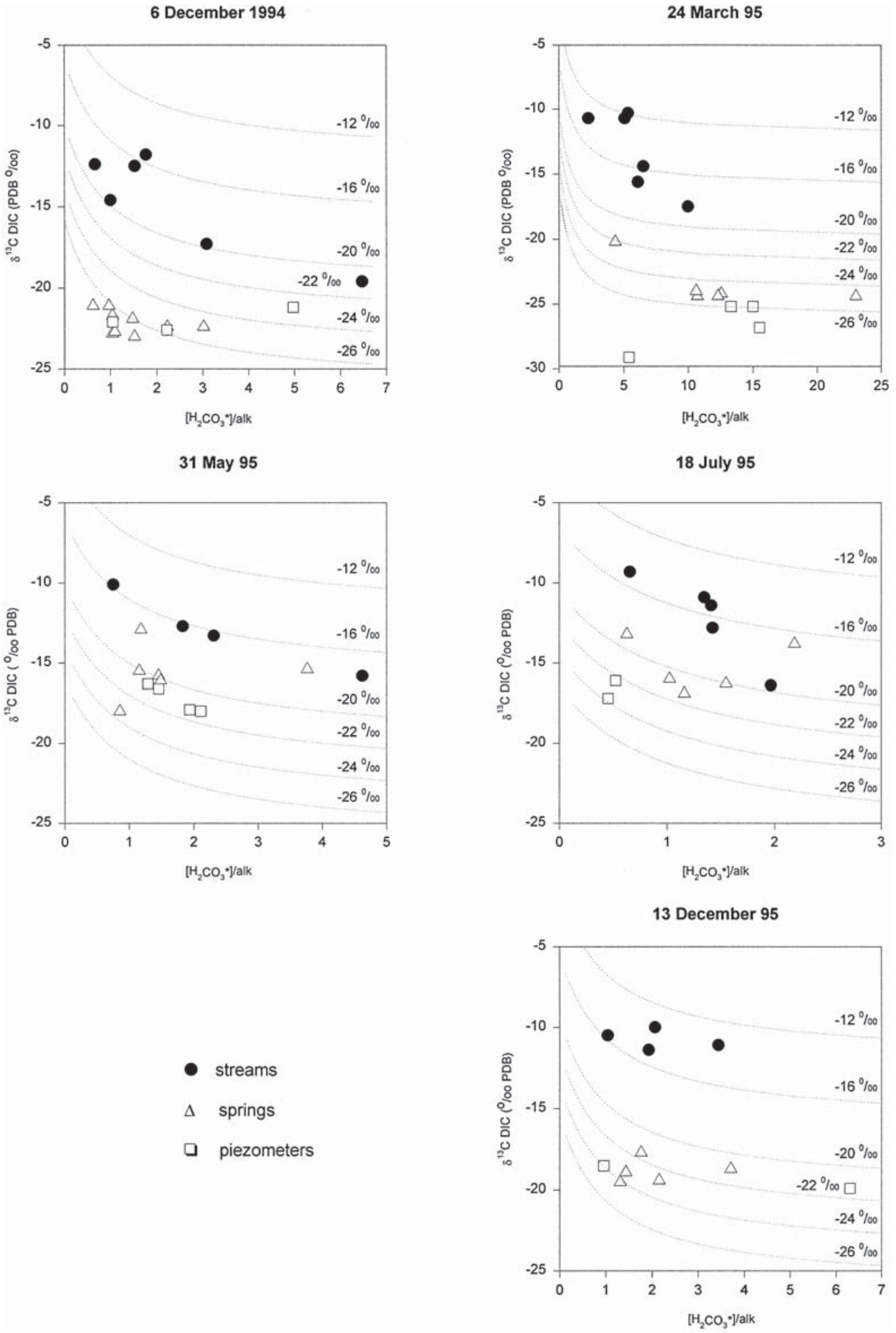
4.1. *Influence of the CO_2 partial pressure (pCO_2)*

The $\delta^{13}C_{DIC}$ values of a given sample can be expressed as a function of the concentrations of aqueous CO_2 ($[H_2CO_3^*]$) and of bicarbonate ions ($[HCO_3^-]$), together with their respective δ^{13}C values ($\delta^{13}C_{H_2CO_3^*}$ and $\delta^{13}C_{HCO_3}$), in the manner (Stumm and Morgan, 1981):

$$\delta^{13}C_{DIC} = \left([H_2CO_3^*] \times \delta^{13}C_{H_2CO_3^*} + [HCO_3^-] \times \delta^{13}C_{HCO_3^-}\right) / ([H_2CO_3] + [HCO_3^-]) \qquad (11)$$

At isotopic equilibrium, $\delta^{13}C_{H_2CO_3^*}$ and $\delta^{13}C_{HCO_3^-}$ are constant and determined by the isotopic composition of soil gaseous CO_2. Thus, the variation of $\delta^{13}C_{DIC}$ is only controlled by the proportions of $H_2CO_3^*$ and HCO_3^- in the solution.

The relationships between the $\delta^{13}C_{DIC}$ in surface water of the Strengbach catchment and the ratio ($[H_2CO_3^*]/[HCO_3^-]$ are plotted in Fig. 7 for the five sampling dates. In the same diagram, we have plotted the theoretical variations of $\delta^{13}C_{DIC}$ in equilibrium with different isotopic composition of soil CO_2, as calculated from Eq. (11) and from the isotopic enrichment factors expressed in Eqs. (8) and (9) of Table 1. Two distinctive groups of points can be clearly observed: (i) the springs and piezometers, in apparent isotopic equilibrium with a ^{13}C depleted gaseous CO_2, and (ii) the stream water, in apparent isotopic equilibrium with ^{13}C enriched gaseous CO_2. Within these two groups, at a given sampling date, the $\delta^{13}C_{DIC}$ values appear to be more or less con-


6 December 1994
24 March 95
31 May 95
18 July 95
13 December 95
δ 13C DIC (PDB ‰)
δ 13C DIC (‰ PDB)
[H2CO3*]/alk
-12 ‰
-16 ‰
-20 ‰
-22 ‰
-24 ‰
-26 ‰
● streams
Δ springs
❑ piezometers

trolled by the relative ratio of $H_2CO_3^*$ to HCO_3^-. Note nevertheless, that the trends of points often cross the theoretical curves, which should indicate that the isotopic composition of the gaseous phase is spatially changing. Such changes are feasible for spring water and piezometers, while, for stream water, non-equilibrium conditions between the gaseous phase and the solution are a more likely alternatives. Indeed, as it can be seen in Table 3, $\delta^{13}C_{DIC}$ values generally increases with increasing distance from springs. This is probably a result of isotopic exchanges between stream DIC with atmospheric CO_2, which occurs together with the evasion of dissolved CO_2 to the atmosphere.

4.2. Influence of soil respiration rates

Comparing the plots for the different sampling dates (Fig. 7), it can be noted that for springs and piezometers the $\delta^{13}C_{DIC}$ seems to be in equilibrium with a gaseous phase which changes with season. In December and March, the DIC appears to be in equilibrium with highly ^{13}C depleted gaseous CO_2 (-25 to -27‰), whereas, in May and July, it seems to be in isotopic equilibrium with CO_2 that has $\delta^{13}C$ around -20‰. This suggests that in winter, soil CO_2 has an isotopic signature similar to that of vegetation, without any fractionation or contamination by atmospheric CO_2, while in summer, the soil CO_2 is fractionated by $+4$ to $+5$‰. These observations are in disagreement with these of Solomon and Cerling (1987) and Cerling et al. (1991) with ^{13}C depleted soil CO_2 accompanying high pCO_2 in summer and atmospheric ^{13}C enrichment and low pCO_2 in winter.

In the Strengbach case, the seasonal variations of $\delta^{13}C$ of the soil CO_2 are better explained by ^{13}C enrichment (up to $+4.4$‰) that is induced by molecular diffusion of gaseous CO_2 throughout the soil pores (Craig, 1954; Dörr and Münnich, 1980; Cerling, 1984; Cerling et al., 1991). This process is more pronounced in summer than in winter, in accord with observations of Dörr and Münnich (1980) and Davidson (1995). In winter, respiration rate being almost equal to zero, molecular diffusion and accompanying isotope fractionation are non-existent. As a result, the isotopic composition of CO_2 is similar to that of the precursor SOM.

4.3. Isotopic equilibration of stream DIC with atmospheric CO_2

Seasonal variations of the $\delta^{13}C_{DIC}$ in the stream at the outlet of the catchment (Fig. 6), are small. We have no explanation for these small oscillations (± 2‰ around -12‰), since we did not observed any clear relationships between the isotopic signal and other parameters, such as the stream discharge, the pH, alkalinity (Fig. 6), pCO_2 in the water, or the concentration of dissolved organic carbon (DOC) that could be partly oxidized in the water.

Fig. 7 shows that the DIC in the stream, in contrast to springs, is not in isotopic equilibrium with the soil CO_2. The general enrichment in ^{13}C of the DIC is caused by the evasion of the isotopically light aqueous CO_2 into the atmosphere and by isotopic equilibration with the atmospheric CO_2 as well. The latter can be modeled by Eq. (11) and by the isotopic fractionation factors expressed as a function of the temperature in Eqs. (8) and (9) (Table 1). The theoretical variations of $\delta^{13}C_{DIC}$ values in the stream can thus be calculated with water temperature weekly recorded in the Strengbach catchment. In our calculations, we have also used the monthly mean $\delta^{13}C$ of the atmospheric CO_2 calculated from the data recorded at Schauinsland, Black Forest, Germany (Levin et al., 1994), about 50 km southeast of the basin. This locality is at a similar altitude and has comparable vegetation cover.

We have calculated two theoretical values of $\delta^{13}C_{DIC}$ with the following assumptions: (i) The entire stream DIC is in isotopic equilibrium with the atmospheric CO_2 (the total equilibrium working hypothesis), and (ii) only the aqueous CO_2 ($H_2CO_3^*$) is in isotopic equilibrium with the atmospheric CO_2 (the partial equilibrium working hypothesis). The resulting theoretical $\delta^{13}C_{DIC}$ are represented in Fig. 8, together with the observed $\delta^{13}C_{DIC}$ values. This

Fig. 7. Evolution of $\delta^{13}C_{DIC}$, vs. $[H_2CO_3^*]$/alkalinity ratio during sampling campaigns, compared to the theoretical evolution of the $\delta^{13}C_{DIC}$ in isotopic equilibrium with different soil CO_2 phases (calculated from Eqs. (8), (9) and (11), see text for explanation).

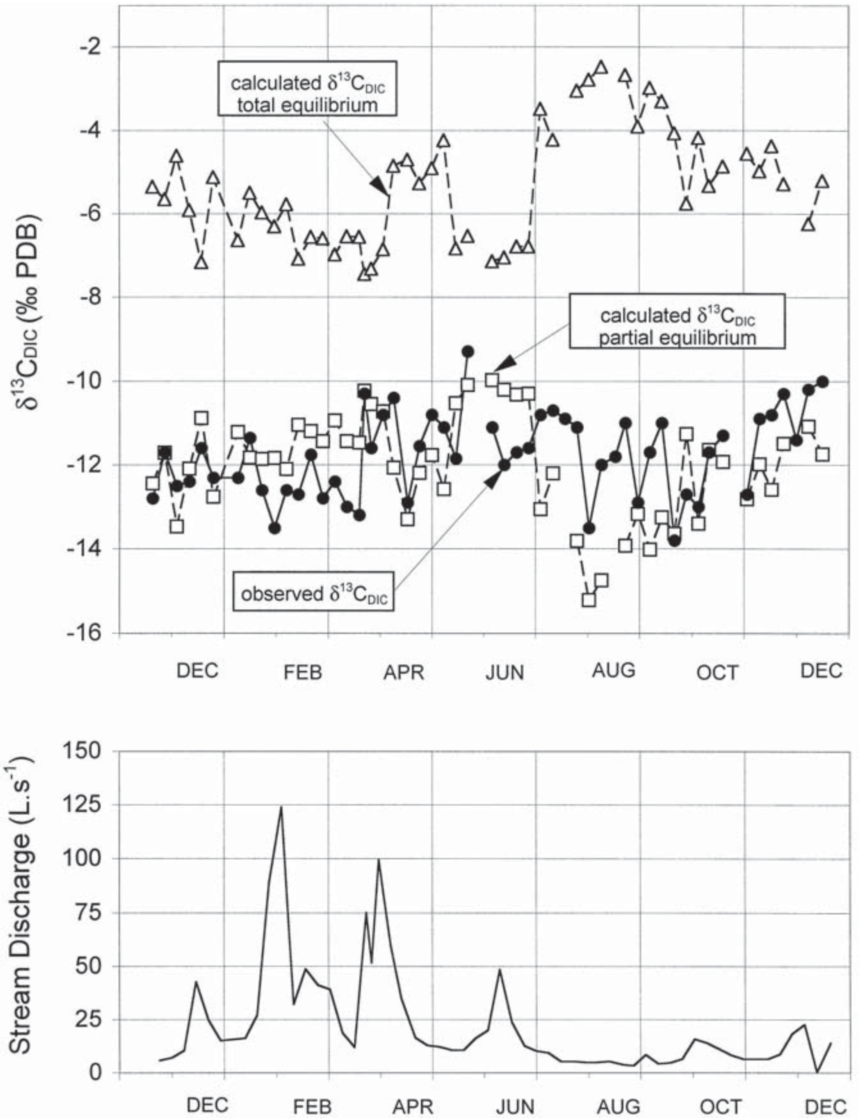


Fig. 8. Temporal fluctuations of $\delta^{13}C_{DIC}$ in the Strengbach stream at the outlet of the catchment December 1994 to December 1995), compared to theoretical predictions of the $\delta^{13}C_{DIC}$ (calculated from Eqs. (8), (9) and (11) and considering total or partial isotopic equilibrium with atmospheric CO_2, see text for explanation).

comparison shows clearly that the partial equilibrium hypothesis is much more consistent with the observations, suggesting that the isotopic exchange between aqueous CO_2 ($H_2CO_3^*$) and atmospheric CO_2 is easier and/or faster than that between bicarbonate ions (HCO_3^-) and atmospheric CO_2. However, this calculated $\delta^{13}C_{DIC}$ is somewhat overestimated for high flow periods (in winter or in June for example) and underestimated for low flow period (in summer). Two hypothesis could explain these differences: (i) the isotopic exchange with atmosphere could be enhanced during low flow periods because of a longer residence time of the water in the stream, whereas a shorter residence time during high flow period would lead to minimize isotopic exchange; (ii) the contribution of the saturated area (bringing light DIC) relative to the rest of the catchment is higher during high flow periods than during low flow periods. Idir et al. (1998) have estimated that the saturated area contributes to 20–30% of the stream discharge at the outlet of the catchment for flood periods. Nevertheless, there are no additional evidence to support either hypothesis.

5. Conclusions

The isotopic composition of the dissolved inorganic carbon (DIC) in the stream at the outlet of the Strengbach catchment is rather uniform, with a mean $\delta^{13}C_{DIC}$ value of $-11.8‰$, despite the fact that the DIC in the Strengbach surface water originates from the soil CO_2 and ultimately from the decay of soil organic matter. The DIC in the spring water is in equilibrium with the soil CO_2, with $\delta^{13}C$ varying from $-20‰$ in the summer to $-26‰$ in winter. This could be a result of, mainly, isotopic fractionation induced by enhanced molecular diffusion of CO_2 through the soil pores in summer due to high respiration rates.

In contrast, the stream DIC is not in isotopic equilibrium with a any specific gas phase, and the ^{13}C enrichment of the stream DIC can reflect evasion of lighter aqueous CO_2 into the atmosphere, coupled with a partial isotopic equilibration with the atmospheric CO_2. Isotopic data suggest that it was the aqueous CO_2 (not all DIC) that equilibrated with atmospheric CO_2. These results clearly show that isotopic composition of the DIC can be significantly affected by atmospheric contamination, without attaining an equilibrium, and this has to be taken into account in interpretation of the riverine $\delta^{13}C_{DIC}$.

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