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# $\delta^{13}\text{C}$ 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  $\text{CO}_2$  generated by oxidation of soil organic matter. The ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in catchment waters is highly variable, from about  $-22\text{‰}$  in the springs and piezometers to about  $-12\text{‰}$  in the stream at the outlet of the catchment. In the springs, pronounced seasonal variations of  $\delta^{13}\text{C}_{\text{DIC}}$  exist, with the DIC in isotopic equilibrium with the soil  $\text{CO}_2$  that has estimated  $\delta^{13}\text{C}$  of about  $-24\text{‰}$  in winter and  $-20\text{‰}$  in summer. These seasonal variations reflect an isotopic fractionation that seems only induced by molecular diffusion of soil  $\text{CO}_2$  in summer. In stream water, seasonal variations are small and the relatively heavy DIC ( $-12\text{‰}$  on average) is a result of isotopic equilibration of the aqueous  $\text{CO}_2$  with atmospheric  $\text{CO}_2$ .

*Keywords:*  $\delta^{13}\text{C}$ ; 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  $\text{CO}_2$ , dissolution of carbonate minerals and atmospheric  $\text{CO}_2$  exchanged through the air–water interface (Yang et al.,

1996). On average, the contribution of soil  $\text{CO}_2$  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  $\text{CO}_2$  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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Its spatial and temporal variations during a complete hydrological cycle enable us to quantify the role of soil and atmospheric CO<sub>2</sub> on the isotopic composition of DIC in a small homogeneous aquatic system.

## 2. Materials and methods

### 2.1. $\delta^{13}\text{C}$ 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<sub>2</sub>(aq)), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. These aqueous compounds can be in contact with gaseous carbon dioxide (CO<sub>2</sub> (g)) and/or carbonate minerals such as calcite (CaCO<sub>3</sub>). 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 (Bourri , 1976):

$$K_H = ([\text{H}_2\text{CO}_3^*] / p\text{CO}_2) = 10^{-1.46} \quad (1)$$

$$K_1 = ([\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3^*]) = 10^{-6.35} \quad (2)$$

$$K_2 = ([\text{CO}_3^{2-}][\text{H}^+] / [\text{HCO}_3^-]) = 10^{-10.33} \quad (3)$$

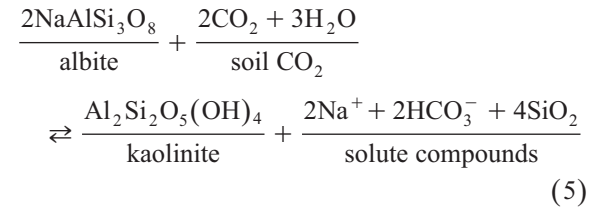
$$K_C = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.47} \quad (4)$$

Note that in Eq. (1), H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> is the analytical sum of aqueous CO<sub>2</sub> (CO<sub>2</sub>aq) and of the true carbonic acid (H<sub>2</sub>CO<sub>3</sub>). It is generally assumed that the concentration of aqueous CO<sub>2</sub> is nearly identical to H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> (Stumm and Morgan, 1981).

The concentration of each species in solution therefore depends on its pH, partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and temperature. In stream water, DIC is mainly composed of HCO<sub>3</sub><sup>-</sup> ions, while in soil solutions, with usually high pCO<sub>2</sub> and low pH values, DIC is mainly composed of H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>.

In small watersheds, HCO<sub>3</sub><sup>-</sup> ions can have two distinct origins: the soil CO<sub>2</sub> and carbonate mineral dissolution. Three alternatives can be considered for the origin of DIC.

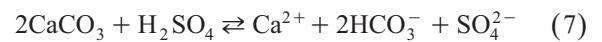
For silicate weathering by carbonic acid, such as albite hydrolysis (see Eq. (5)), DIC originates solely from soil CO<sub>2</sub>.



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<sub>2</sub>.



For carbonate dissolution by acids other than H<sub>2</sub>CO<sub>3</sub> (e.g., sulfuric or organic acids), DIC originates solely from carbonate minerals (Eq. (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<sub>2</sub>.

### 2.1.2. Isotopic composition ( $\delta^{13}\text{C}$ ) of soil CO<sub>2</sub>

In the case of silicate rock weathering (Eq. (5)), the isotopic composition of DIC should reflect that of soil CO<sub>2</sub> that is produced by decomposition of soil organic matter (SOM) and by root respiration. Several processes lead the isotopic composition of soil CO<sub>2</sub> to be slightly different from that of SOM.

The  $\delta^{13}\text{C}$  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  $^{13}\text{C}$  (about 1 to 4‰) during its mineralization. As a result, the  $\delta^{13}\text{C}$  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  $^{13}\text{C}$  of the residual soil CO<sub>2</sub>. 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  $\delta^{13}\text{C}$  value for SOM of  $-25\%$ , the maximum  $\delta^{13}\text{C}$  of soil CO<sub>2</sub> can be estimated to about  $-21\%$ .

Alternatively, soil CO<sub>2</sub> 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  $\delta^{13}\text{C}$  of soil CO<sub>2</sub> and its associated partial pressures ( $p\text{CO}_2$ ), for sev-

eral soils in temperate climate and covered by C3 plants. In summer, the rate of SOM oxidation is high, inducing high  $p\text{CO}_2$  in soils and preventing atmospheric CO<sub>2</sub> from penetrating the soil. As a result, the  $\delta^{13}\text{C}$  of soil CO<sub>2</sub> is low, close to that of SOM. In contrast, the soil biologic activity is low in winter, permitting atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C}$  of about  $-8\%$ ) to penetrate the soil, leading to an enrichment in  $^{13}\text{C}$ . As a consequence, the  $\delta^{13}\text{C}$  of soil CO<sub>2</sub> 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<sub>2</sub>

The isotopic fractionation factors between the different carbonate species dissolved in continental water and gaseous CO<sub>2</sub> 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 ( $\epsilon$ ) and the temperature ( $T$ ) are shown in Table 1.

Potential variations of carbon isotopic composition ( $\delta^{13}\text{C}$ ) in an aqueous system are shown in Fig. 1. For DIC originating solely from soil CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> ions should be enriched in  $^{13}\text{C}$  by about 8 to 10‰ (Table 1), whereas the aqueous CO<sub>2</sub> should be depleted by about 1‰. In contrast, HCO<sub>3</sub><sup>-</sup> ions from dissolution of carbonate rocks should not show any fractionation relative to precursor carbonate minerals. If so, for catchments covered by C3 plants ( $\delta^{13}\text{C} = -26\%$ ), with no contamination of the soil CO<sub>2</sub> by atmospheric CO<sub>2</sub> and laying on non-carbonate rocks, the isotopic composition of DIC in

Table 1

Isotopic enrichment factors ( $\epsilon$ ) between gaseous CO<sub>2</sub> and dissolved carbonate species (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) as a function of temperature (in °C) (from Zhang et al., 1994)

Relationships between isotopic enrichment factors ( $\epsilon$ , in ‰) and temperature ( $T$ , in °C)		$\epsilon$ in ‰	
		at 5°C	at 25°C
$\epsilon_{\text{CO}_2\text{g}(\text{H}_2\text{CO}_3^*)} = (0.0049 \times T) - 1.31$	(8)	-1.29	-1.19
$\epsilon_{\text{CO}_2\text{g}(\text{HCO}_3^-)} = (-0.1141 \times T) + 10.78$	(9)	+10.21	+7.93
$\epsilon_{\text{CO}_2\text{g}(\text{CO}_3^{2-})} = (-0.052 \times T) + 7.22$	(10)	+6.96	+5.92

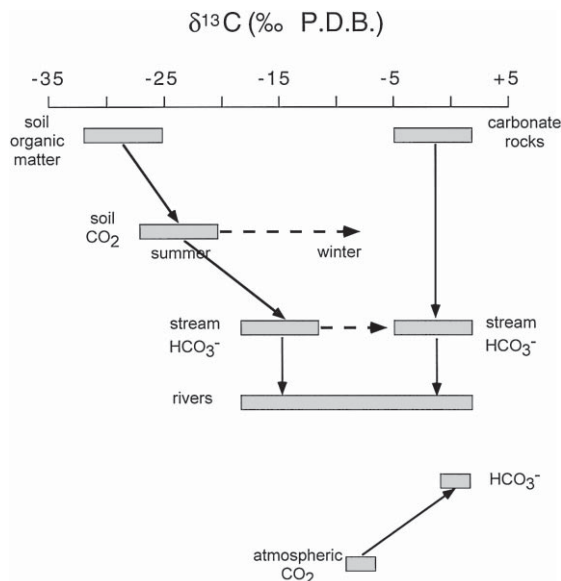


Fig. 1. Potential variations of carbon isotopic composition in aqueous systems (modified from Pawellek and Veizer, 1994).

stream water, mainly  $\text{HCO}_3^-$  ions, should vary between  $-16$  to  $-19\text{‰}$ .

Finally, if the DIC is completely in isotopic equilibrium with atmospheric  $\text{CO}_2$ , its isotopic signature should vary between  $0$  and  $+2\text{‰}$  (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  $\text{CO}_2$ .

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  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  and the alkalinity is quite low (pH = 6.10 and  $\text{alk} = 36.0 \mu\text{eq l}^{-1}$ , 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  $0.45 \mu\text{m}$  Millipore membrane, applying a small underpressure with a hand-operated vacuum pump. The

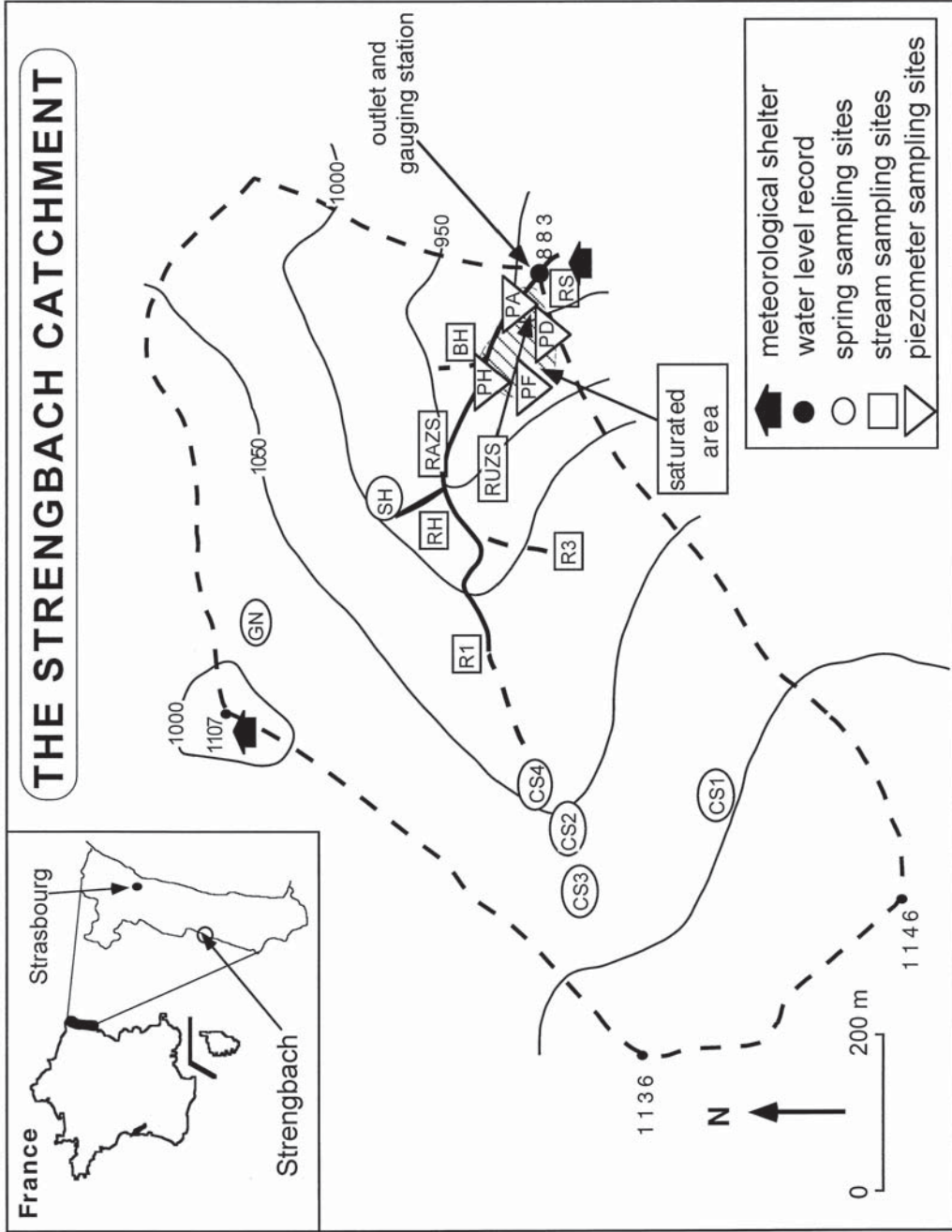


Fig. 2. Location and description of the Strengbach catchment.



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  $\text{HgCl}_2$  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  $+5^\circ\text{C}$  prior to analysis.

The  $\delta^{13}\text{C}_{\text{DIC}}$  was measured at the Centre de Géochimie de la Surface, in Strasbourg, following the procedure of Kroopnick et al. (1970). Phosphoric

acid ( $\text{H}_3\text{PO}_4$ ) is added to the sample inside a vacuum line and the evolved  $\text{CO}_2$  is purified and trapped with liquid nitrogen in a glass tube. The isotopic composition of this gaseous  $\text{CO}_2$  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  $\pm 0.2\%$ . 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.

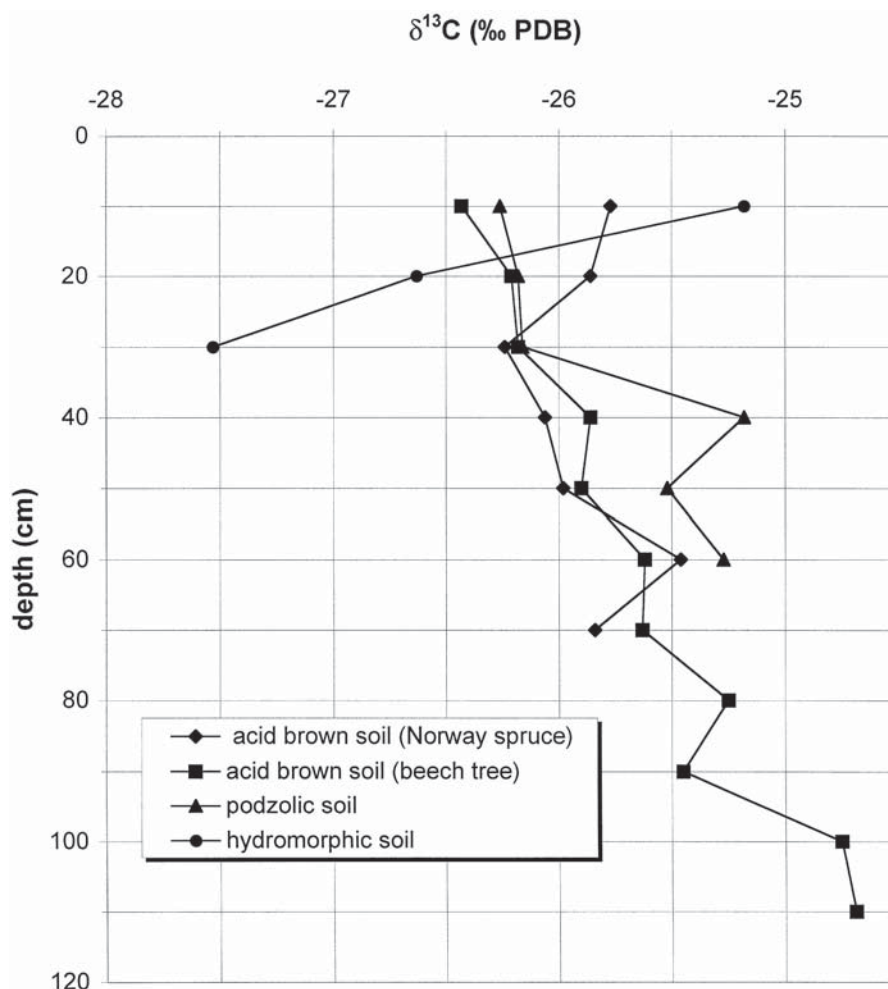


Fig. 3. Variation of  $\delta^{13}\text{C}$  for the soil organic matter in the different soil profiles of the Strengbach catchment.

### 3. Results

#### 3.1. $\delta^{13}\text{C}$ 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  $\delta^{13}\text{C}$  of  $-24.7$  to  $-26.4\text{‰}$  for the acid brown and the podzolic soils and a small enrichment in  $^{13}\text{C}$  with increasing depth (Fig. 3). This  $^{13}\text{C}$  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  $^{13}\text{C}$  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 ( $\delta^{13}\text{C} = -25.2\text{‰}$ ), 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

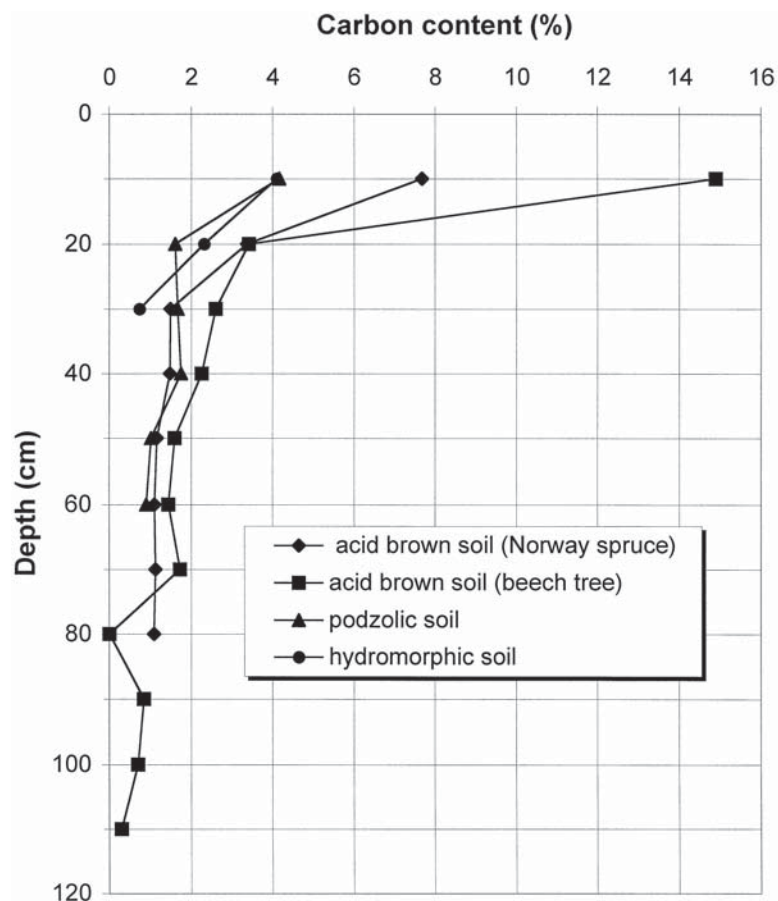


Fig. 4. Variation of carbon content of the soil organic matter in the different soil profiles of the Strengbach catchment.



decomposition of SOM produces very depleted methane ( $\delta^{13}\text{C}$  around  $-50\text{‰}$ ) but relatively enriched  $\text{CO}_2$  ( $\delta^{13}\text{C}$  from  $-9$  to  $-12\text{‰}$ ). Such processes lead to a decrease in the  $\delta^{13}\text{C}$  of the accumu-

lated SOM ( $-29.2\text{‰}$ ) relative to the fresh organic matter ( $-26.8\text{‰}$ ). Additional studies are required in order to establish to what extent the soil  $\text{CO}_2$  could be isotopically contaminated by  $\text{CH}_4$ .

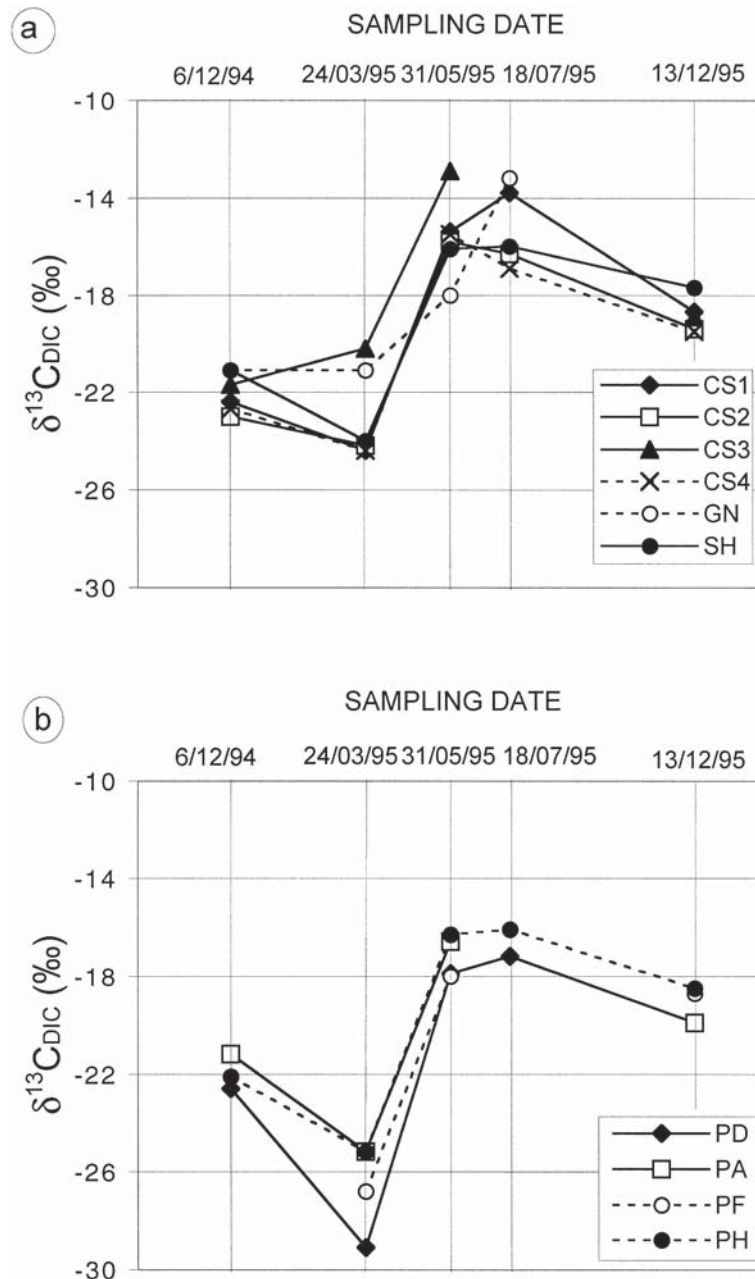


Fig. 5. Temporal fluctuations of  $\delta^{13}\text{C}_{\text{DIC}}$  in the springs (CS1, CS2, CS3, CS4, GN, SH) and the piezometers (PA, PD, PF, PH) of the Strengbach catchment (see Fig. 2 for location of sampling sites).

Assuming an isotopic enrichment of +1 to +4‰ induced by molecular diffusion of CO<sub>2</sub> in soil pores (see above), the  $\delta^{13}\text{C}$  of the soil CO<sub>2</sub> 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. $\delta^{13}\text{C}$ 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  $\delta^{13}\text{C}_{\text{DIC}}$  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<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, isotopically equilibrated with light soil CO<sub>2</sub>, relative to HCO<sub>3</sub><sup>-</sup> ions. Nevertheless, the  $\delta^{13}\text{C}_{\text{DIC}}$  values shows significant, station independent, seasonal variations (Fig. 5). In winter 1994/95, the  $\delta^{13}\text{C}_{\text{DIC}}$  values vary on average between -26.6 and -23.2‰, that is in the estimated range of the soil CO<sub>2</sub>. Subsequently, in the late

spring and in summer, DIC becomes enriched in <sup>13</sup>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  $\delta^{13}\text{C}_{\text{DIC}}$  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<sub>2</sub>CO<sub>3</sub><sup>\*</sup> vs. HCO<sub>3</sub><sup>-</sup>), are similar in spring and in piezometers. Whatever the explanation, the enrichment in <sup>13</sup>C (about 7–8‰) between winter and summer samples, is also recorded in piezometers as well.

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

DIC in stream water is clearly enriched in <sup>13</sup>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  $\delta^{13}\text{C}_{\text{DIC}}$  ranges between -13.8‰ and -9.3‰

Table 2  
Average values and ranges of  $\delta^{13}\text{C}_{\text{DIC}}$ , HCO<sub>3</sub><sup>-</sup> concentrations and pCO<sub>2</sub> in springs and piezometers for 5 sampling campaigns

Sampling date	Number of sample			$\delta^{13}\text{C}_{\text{DIC}}$		HCO <sub>3</sub> <sup>-</sup> (meq l <sup>-1</sup> )		log pCO <sub>2</sub> (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

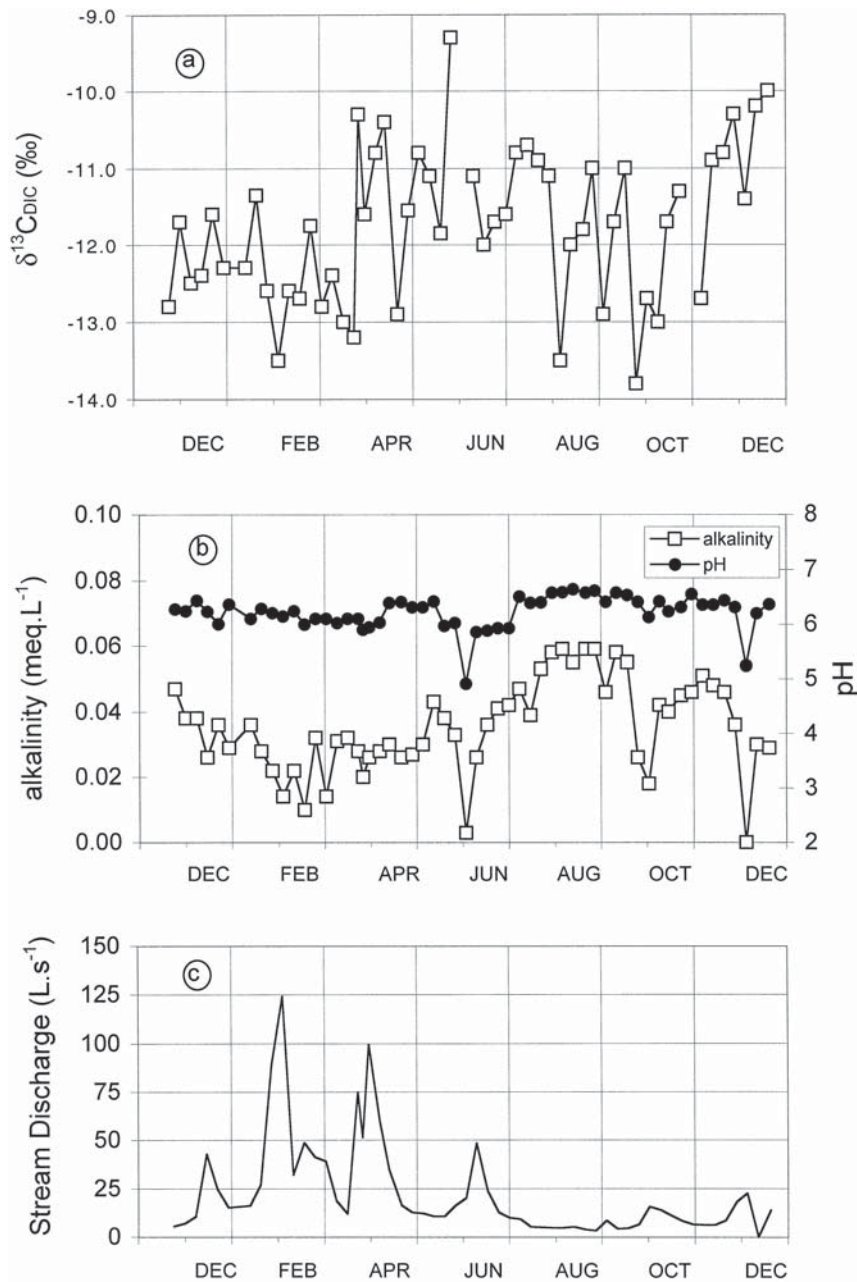


Fig. 6. Weekly fluctuations (22/11/94 to 13/12/95) of (a)  $\delta^{13}C_{DIC}$ , (b) alkalinity and pH and (c) stream discharge in the Strengbach stream at the outlet from the catchment (site RS).

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  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\text{HCO}_3^-$  concentrations,  $p\text{CO}_2$  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		$\delta^{13}\text{C}_{\text{DIC}}$ (‰ PDB)	$\text{HCO}_3^-$ ( $\text{meq l}^{-1}$ )	$\log p\text{CO}_2$ (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 $\delta^{13}\text{C}$ values of DIC

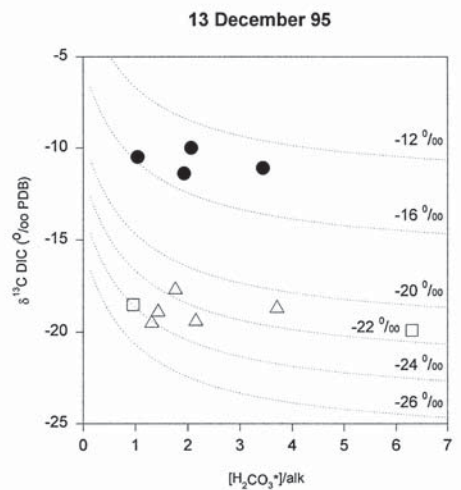
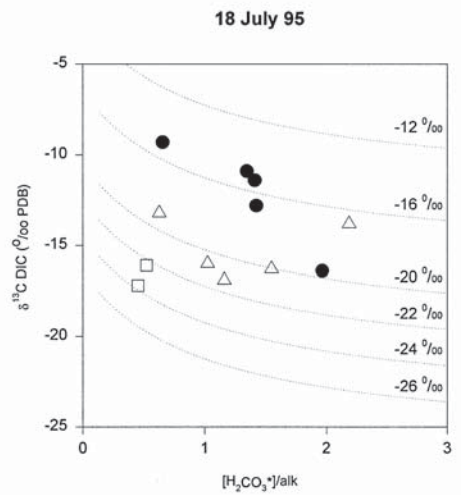
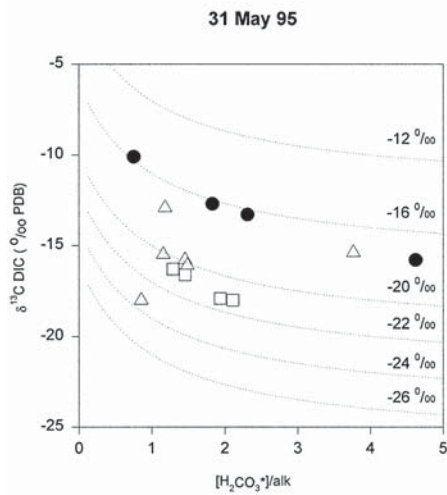
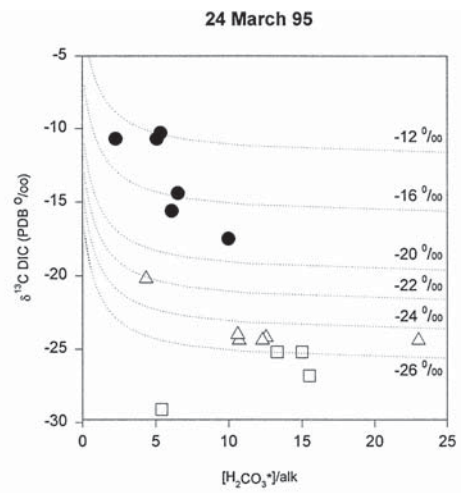
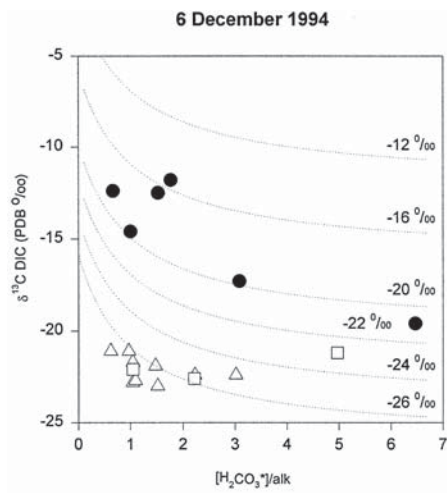
##### 4.1. Influence of the $\text{CO}_2$ partial pressure ( $p\text{CO}_2$ )

The  $\delta^{13}\text{C}_{\text{DIC}}$  values of a given sample can be expressed as a function of the concentrations of aqueous  $\text{CO}_2$  ( $[\text{H}_2\text{CO}_3^*]$ ) and of bicarbonate ions ( $[\text{HCO}_3^-]$ ), together with their respective  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3^*}$  and  $\delta^{13}\text{C}_{\text{HCO}_3^-}$ ), in the manner (Stumm and Morgan, 1981):

$$\delta^{13}\text{C}_{\text{DIC}} = \left( [\text{H}_2\text{CO}_3^*] \times \delta^{13}\text{C}_{\text{H}_2\text{CO}_3^*} + [\text{HCO}_3^-] \times \delta^{13}\text{C}_{\text{HCO}_3^-} \right) / ([\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-]) \quad (11)$$

At isotopic equilibrium,  $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3^*}$  and  $\delta^{13}\text{C}_{\text{HCO}_3^-}$  are constant and determined by the isotopic composition of soil gaseous  $\text{CO}_2$ . Thus, the variation of  $\delta^{13}\text{C}_{\text{DIC}}$  is only controlled by the proportions of  $\text{H}_2\text{CO}_3^*$  and  $\text{HCO}_3^-$  in the solution.

The relationships between the  $\delta^{13}\text{C}_{\text{DIC}}$  in surface water of the Strengbach catchment and the ratio ( $[\text{H}_2\text{CO}_3^*]/[\text{HCO}_3^-]$ ) are plotted in Fig. 7 for the five sampling dates. In the same diagram, we have plotted the theoretical variations of  $\delta^{13}\text{C}_{\text{DIC}}$  in equilibrium with different isotopic composition of soil  $\text{CO}_2$ , 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  $^{13}\text{C}$  depleted gaseous  $\text{CO}_2$ , and (ii) the stream water, in apparent isotopic equilibrium with  $^{13}\text{C}$  enriched gaseous  $\text{CO}_2$ . Within these two groups, at a given sampling date, the  $\delta^{13}\text{C}_{\text{DIC}}$  values appear to be more or less con-



trolled by the relative ratio of  $\text{H}_2\text{CO}_3^*$  to  $\text{HCO}_3^-$ . 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,  $\delta^{13}\text{C}_{\text{DIC}}$  values generally increases with increasing distance from springs. This is probably a result of isotopic exchanges between stream DIC with atmospheric  $\text{CO}_2$ , which occurs together with the evasion of dissolved  $\text{CO}_2$  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  $\delta^{13}\text{C}_{\text{DIC}}$  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  $^{13}\text{C}$  depleted gaseous  $\text{CO}_2$  ( $-25$  to  $-27\%$ ), whereas, in May and July, it seems to be in isotopic equilibrium with  $\text{CO}_2$  that has  $\delta^{13}\text{C}$  around  $-20\%$ . This suggests that in winter, soil  $\text{CO}_2$  has an isotopic signature similar to that of vegetation, without any fractionation or contamination by atmospheric  $\text{CO}_2$ , while in summer, the soil  $\text{CO}_2$  is fractionated by  $+4$  to  $+5\%$ . These observations are in disagreement with these of Solomon and Cerling (1987) and Cerling et al. (1991) with  $^{13}\text{C}$  depleted soil  $\text{CO}_2$  accompanying high  $p\text{CO}_2$  in summer and atmospheric  $^{13}\text{C}$  enrichment and low  $p\text{CO}_2$  in winter.

In the Strengbach case, the seasonal variations of  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  are better explained by  $^{13}\text{C}$  enrichment (up to  $+4.4\%$ ) that is induced by molecular diffusion of gaseous  $\text{CO}_2$  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 be-

ing almost equal to zero, molecular diffusion and accompanying isotope fractionation are non-existent. As a result, the isotopic composition of  $\text{CO}_2$  is similar to that of the precursor SOM.

#### 4.3. Isotopic equilibration of stream DIC with atmospheric $\text{CO}_2$

Seasonal variations of the  $\delta^{13}\text{C}_{\text{DIC}}$  in the stream at the outlet of the catchment (Fig. 6), are small. We have no explanation for these small oscillations ( $\pm 2\%$  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),  $p\text{CO}_2$  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  $\text{CO}_2$ . The general enrichment in  $^{13}\text{C}$  of the DIC is caused by the evasion of the isotopically light aqueous  $\text{CO}_2$  into the atmosphere and by isotopic equilibration with the atmospheric  $\text{CO}_2$  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  $\delta^{13}\text{C}_{\text{DIC}}$  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  $\delta^{13}\text{C}$  of the atmospheric  $\text{CO}_2$  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  $\delta^{13}\text{C}_{\text{DIC}}$  with the following assumptions: (i) The entire stream DIC is in isotopic equilibrium with the atmospheric  $\text{CO}_2$  (the total equilibrium working hypothesis), and (ii) only the aqueous  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3^*$ ) is in isotopic equilibrium with the atmospheric  $\text{CO}_2$  (the partial equilibrium working hypothesis). The resulting theoretical  $\delta^{13}\text{C}_{\text{DIC}}$  are represented in Fig. 8, together with the observed  $\delta^{13}\text{C}_{\text{DIC}}$  values. This

Fig. 7. Evolution of  $\delta^{13}\text{C}_{\text{DIC}}$ , vs.  $[\text{H}_2\text{CO}_3^*]/\text{alkalinity}$  ratio during sampling campaigns, compared to the theoretical evolution of the  $\delta^{13}\text{C}_{\text{DIC}}$  in isotopic equilibrium with different soil  $\text{CO}_2$  phases (calculated from Eqs. (8), (9) and (11), see text for explanation).



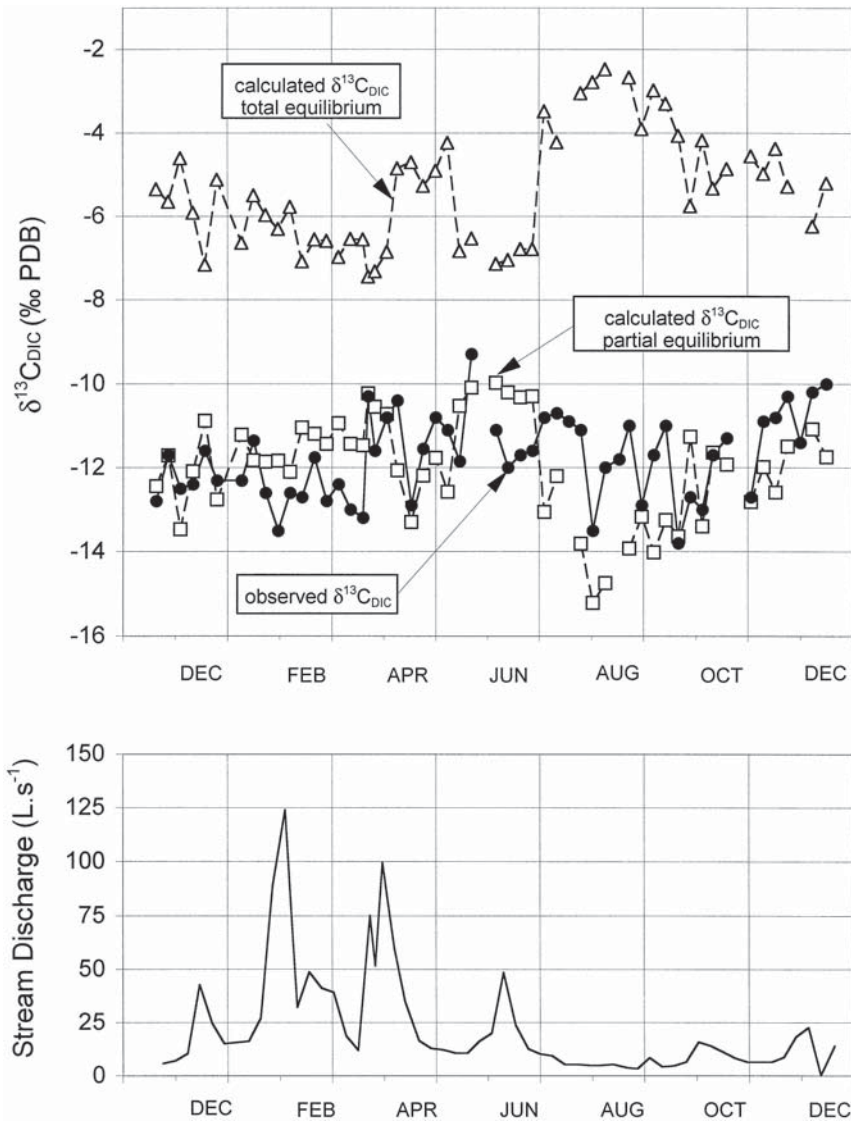


Fig. 8. Temporal fluctuations of  $\delta^{13}\text{C}_{\text{DIC}}$  in the Strengbach stream at the outlet of the catchment December 1994 to December 1995), compared to theoretical predictions of the  $\delta^{13}\text{C}_{\text{DIC}}$  (calculated from Eqs. (8), (9) and (11) and considering total or partial isotopic equilibrium with atmospheric  $\text{CO}_2$ , 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  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3^*$ ) and atmospheric  $\text{CO}_2$  is easier and/or faster than that between bicarbonate ions ( $\text{HCO}_3^-$ ) and atmospheric  $\text{CO}_2$ . However, this calculated  $\delta^{13}\text{C}_{\text{DIC}}$  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  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-11.8\text{‰}$ , despite the fact that the DIC in the Strengbach surface water originates from the soil  $\text{CO}_2$  and ultimately from the decay of soil organic matter. The DIC in the spring water is in equilibrium with the soil  $\text{CO}_2$ , with  $\delta^{13}\text{C}$  varying from  $-20\text{‰}$  in the summer to  $-26\text{‰}$  in winter. This could be a result of, mainly, isotopic fractionation induced by enhanced molecular diffusion of  $\text{CO}_2$  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  $^{13}\text{C}$  enrichment of the stream DIC can reflect evasion of lighter aqueous  $\text{CO}_2$  into the atmosphere, coupled with a partial isotopic equilibration with the atmospheric  $\text{CO}_2$ . Isotopic data suggest that it was the aqueous  $\text{CO}_2$  (not all DIC) that equilibrated with atmospheric  $\text{CO}_2$ . 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  $\delta^{13}\text{C}_{\text{DIC}}$ .

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