VARIATIONS IN THE ISOTOPIC COMPOSITION OF DISSOLVED INORGANIC CARBON IN THE UNSATURATED ZONE OF A SEMI-ARID REGION

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ABSTRACT. A study of water and carbon isotopes was conducted in a bare plot in the unsaturated zone of the Yatir Forest in the northern Negev of Israel. Sediment cores were collected in three different seasons. Measurements include profiles of mineralogy, moisture and its $\delta^{18}O$ and tritium content, dissolved inorganic carbon (DIC) and its $\delta^{13}C$ (‰) and $\Delta^{14}C$ (‰) content, and $\delta^{13}C$ (‰) and $\Delta^{14}C$ (‰) in the solid sediment. The profiles of moisture and $\delta^{18}O$ in the cores show clearly the effect of evaporation. The tritium profile indicates infiltration of water (0.11 m yr^{-1}). The source of carbon in the DIC is CO_2 released by biotic activity through roots of trees and of seasonal plants, which show seasonal variations, and by decay of organic debris. The $\delta^{13}C$ (‰) profiles show clearly the chemical transition from dissolved CO_2 ($\delta^{13}C = -22‰$) to bicarbonate ($\delta^{13}C = -14‰$). At greater depth ($-11.3‰$), the $\delta^{13}C$ becomes similar to the $\delta^{13}C$ in the aquifer below ($-12.5‰$). The effect of secondary processes is evident in the profile of $\Delta^{14}C$ in the DIC. It shows a clear decrease with depth due to exchange with the sediment at a rate of 10% yr^{-1}. Precipitation of carbon from the DIC on the sediment is 1.1 mg C L$_{sed}$$^{-1}$ yr^{-1}, negligible compared to the 28 g C in 1 L$_{sed}$. In the solid sediment, there is a gradient in $\Delta^{14}C_{carb}$ at the top meter. The net precipitation of ^{14}C from the DIC on the sediment (0.25 to 1.1‰ yr^{-1}), corrected for decay, cannot be observed in the deeper sediment. The presence of ^{14}C in the top 1 m of the sediment is explained by two possible processes: accumulation of ^{14}C-tagged dust (~0.05 mm yr^{-1}) and/or long-term cumulative precipitation from the DIC.

INTRODUCTION

The unsaturated zone (USZ) is the interface between rainwater above and aquifer water below. It is composed of three phases: solid, liquid, and gas. In arid regions, its thickness may reach hundreds of meters (Tindall and Kunkel 1999). In Israel, the thickness is several meters. In the USZ, chemical processes between the three phases define the chemical composition of the water at the entrance to an aquifer (Tindall and Kunkel 1999).

The carbon system in the USZ of the coastal aquifer of Israel was studied by Carmi et al. (2009). It was shown that the concentration and the isotopic composition of dissolved inorganic carbon (DIC) in the rainwater that had entered the USZ and passes to the aquifer is defined by interactions between the CO_2 gas from roots and from decay of organic debris, rainwater, and the carbonate of the solid phase. A gradient of the DIC with depth in the USZ was interpreted as sequestration of atmospheric CO_2 in the USZ (Moinester et al. 2014).

The climate in a significant part of Israel is semi-arid. The results of the study of the carbon system in the USZ of the coastal region by Carmi et al. (2009) justified a similar study in the semi-arid, forested region of Yatir. A thorough study of CO_2 in the gas phase in the USZ of Yatir has already been published (Carmi et al. 2013). The aim of the present study is thus to understand the processes that affect the carbon content and its isotopic composition in the liquid and solid phases of the unsaturated zone of a semi-arid region with rainfall lower than that of the coastal region.

SITE DESCRIPTION

The Yatir Forest (31°20′N, 35°03′E, 650 m above sea level) is located in a semi-arid zone (280 mm yr^{-1} precipitation) on the southwestern flanks of the Judea Mountains of Israel (Figure 1a). The forest was planted by the Jewish National Fund in the late 1960s and it is the site of the Yatir Bio-Ecological Station of the Weizmann Institute of Science (WIS), which was established in spring 2000 (Grünzweig et al. 2003). The present study of the soil sediments of the USZ was carried out

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in a bare 20 × 20 m plot (Figure 1b) in the forest, situated some 100 m to the east of the Yatir Bio-Ecological Station. The Yatir Forest was within ~5 m of the study area. The topmost unconsolidated part of the unsaturated zone (USZ) in Yatir extends from the land surface to a depth of up to 5 m. It overlies the carbonate USZ of the mountain aquifer. The USZ in Yatir Forest has no relation to the underlying carbonate rock.
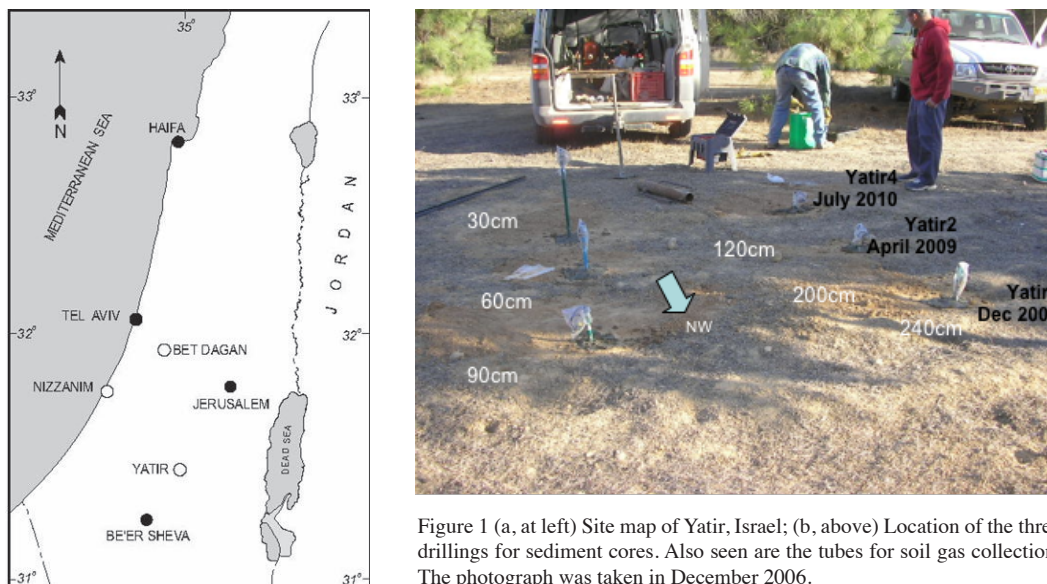

Figure 1 (a, at left) Site map of Yatir, Israel; (b, above) Location of the three drillings for sediment cores. Also seen are the tubes for soil gas collection. The photograph was taken in December 2006.

The USZ of Yatir consists of three phases, all of which contain carbon: the solid phase is composed of minerals, some of which are carbonaceous and organic detritus; the liquid phase, which contains DIC; and the gaseous phase, which includes CO_2. Some of the CO_2 originates from the ambient atmosphere, but a greater part is generated within the USZ itself from respiration at the root zone and from decay of solid organic matter. The abundance of CO_2 in the gas phase of the USZ in Yatir varies between 400 and 9000 parts per million (ppm) (Carmi et al. 2013), which is similar to the global CO_2 concentration in the USZ of 400 to 10,000 ppm (Tindall and Kunkel 1999). Some of the CO_2 in the USZ dissolves in the infiltrating rainwater to form DIC, which interacts with the solid sediments. Eventually, water from the USZ penetrates all the way to the underlying aquifer.

METHODS

In December 2006 and April 2009, two 3-m-long sediment cores were collected from the USZ of a bare plot in the Yatir Forest with a sampling resolution of 0.5 m. In July 2010, a third sediment core 4.4 m long was similarly taken with a sampling resolution of 0.3 m. The spacing between the cores was less than 1 m (Figure 1b). In the field, following the collection, the sediments were packed in two tightly closed plastic bags, one inside the other. The samples were then stored in a refrigerator in the Department of Environmental Science and Energy Research at the WIS (ESER). Processing of the samples was carried out in a lab at ESER.

The moisture content of the sediment and the CO_2 derived from the DIC species in the soil water were obtained by vacuum extraction to total dryness (Carmi et al. 2007). The dissolved inorganic carbon content of the soil water (DIC_{sed}, mmol C L^{-1}) was calculated by dividing the amount of collected CO_2 by the amount of collected water and normalized to 1 L of sediment, mmol C L_{sed}^{-1}.

The vacuum extraction method excludes further analysis of porewater chemical composition. Therefore, in the absence of data on the ionic composition of the soil water, chemical calculations cannot be performed and additional information on the USZ porewater chemistry is lost.

In the first two cores, the $\delta^{13}C$ (‰) content of the DIC was measured in a Finnigan Mat 250 mass spectrometer, at ESER. The $\delta^{18}O$ (‰) of the water was measured using a Carlo Erba 1108 elemental analyzer coupled to a continuous-flow micromass isotope ratio spectrometer (Klein et al. 2005). ^{14}C in the DIC was measured at the NSF-Arizona AMS laboratory, which also measured the $\delta^{13}C$ (‰) in the third core. Tritium was measured in the Radiation Safety Division of the Soreq Nuclear Research Centre using ultra-low background scintillation counters.

An aliquot of the sediment samples was submitted to the Israel Geological Survey (IGS) for semi-quantitative mineralogical analysis using X-ray diffraction (XRD). From another aliquot, the inorganic carbon isotopes (^{13}C and ^{14}C) in the solid phase were prepared for analysis and then submitted for measurement at the NSF-Arizona AMS laboratory.

RESULTS AND DISCUSSION

The isotopic compositions of the water and of the DIC_{sed} in the three cores are presented in Table 1, Figures 3a–c, and Figures 4a–c. The carbon isotopic composition of the solid sediment is presented in Table 2 and in Figure 4d.

Mineralogy of the Sediment

The mineralogy of the USZ consists of quartz, clay, and carbonate in various proportions, with quartz being the major component along most of the profile (Figure 2). The sediments resemble the loess that is common in many parts of the northern Negev of Israel (Yaalon 1974). The porosity of the USZ is uniform (53%) and the bulk density is 1.26 g mL^{-1}. The organic matter content was measured in a sample from a depth of 1.8 m and was found to be 1.3%.
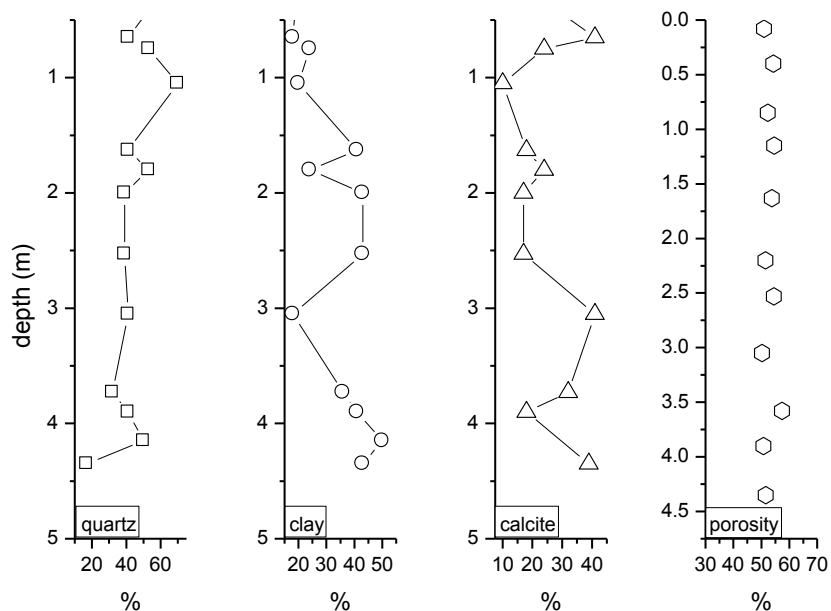

Figure 2 Porosity and semi-quantitative sedimentology (%) in the July 2010 core of Yatir

Moisture in the USZ and Its Evaporation

The three sediment cores were collected in three different seasons: winter (December 2006), spring (April 2009), and summer (July 2010). The 3 yr between the first and the second cores (respectively, 2006 and 2009) is due to logistic difficulties, but it was assumed that the changes will be minor. An expected difference between seasons is the reason for timing the collection of cores in December, April, and July. The range of moisture content in theses cores varied between 2.8% at 0.08 m and 18.8% at 4.35 m. The profiles of moisture in the USZ reflect seasonal changes between infiltration of rainwater into it and the evaporation of water out of it to a depth of about 0.5 m (Figure 3a). Between 2000 and 2010, the average annual rainfall in Yatir was 280 mm (www.ims.gov.il), justifying the assumptions made above about the annual changes being minor and the seasonal changes being significant. However, this rainfall is not distributed evenly in time. There are many events of less than 5 mm rainfall and quite a few storms of more than 15 mm rainfall. Thus, in April 2009, following 136 mm of rainfall in February and March, an increase in moisture is seen at the top of the profile (Figure 3a and Table 1). In the winter of 2010, there were heavy rains in January and February, totaling 200 mm, which infiltrated the USZ. Yet, after 3 months of hot, rainless summer, the moisture at the top of the July 2010 sediment core (above 30 cm) is very low, suggesting intense summer evaporation (Figure 3a and Table 1). Below the depth of 0.5 m, the moisture has apparently escaped evaporation and it increases with depth. At the deepest point of the July 2010 core (4.35 m), there is an increase in the moisture that may suggest accumulation of water (Figure 3a and Table 1). In the winter of 2006, between mid-October and December, there were three rainstorms (17, 14, and 34 mm). In the upper part of the December 2006 profile (Figure 3a and Table 1), the moisture content indicates evaporation, but it is less intensive than that in the summer (July 2010 profile). The lower evaporation can be due to these storms, which reduced but did not eradicate its effect completely.
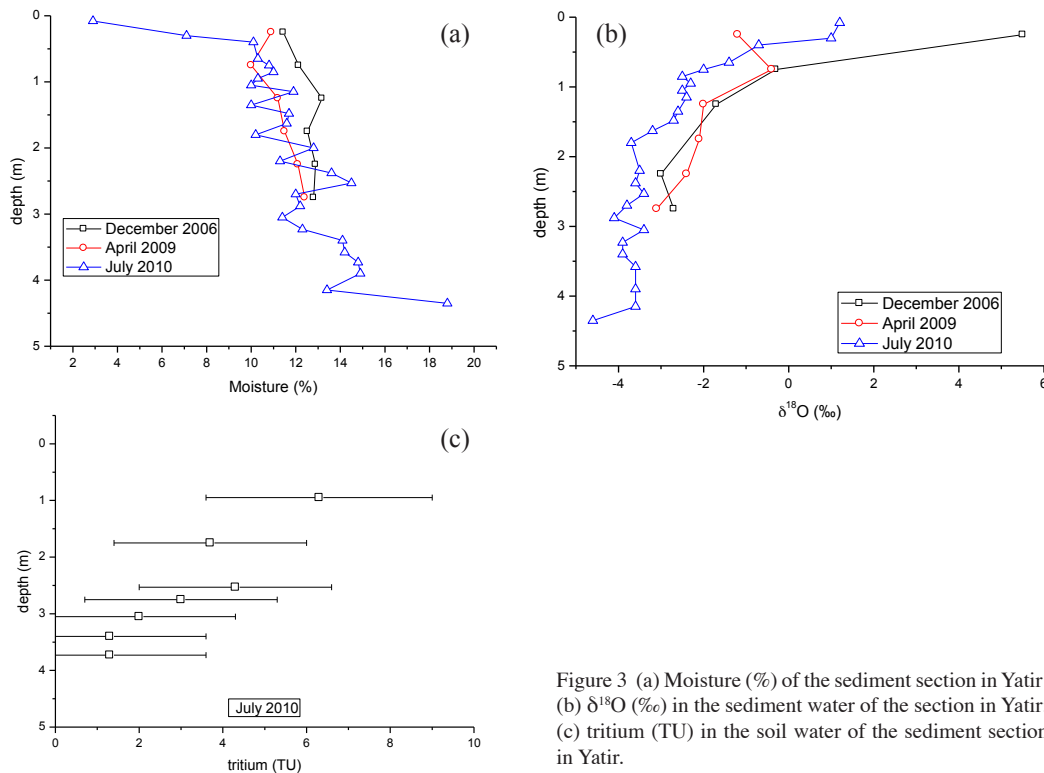

Figure 3 (a) Moisture (%) of the sediment section in Yatir; (b) $\delta^{18}O$ (‰) in the sediment water of the section in Yatir; (c) tritium (TU) in the soil water of the sediment section in Yatir.

δ18O in the Moisture of the USZ and the Effect of Evaporation

Evaporation fractionates oxygen isotopes, making the $\delta^{18}O$ heavier (more positive) in the residual water. This can be readily seen at the top of the section (Figure 3b and Table 1) in the December 2006 profile and is less pronounced in the July 2010 profile. The influence of evaporation upon the $\delta^{18}O$ profiles can be observed down to about 1.5 m, which is deeper than the depth observed in the moisture content (0.5 m). This difference indicates that $\delta^{18}O$ is more sensitive than moisture content for observing the effect of evaporation.

Table 1 Dissolved carbon and water isotopic compositions in three drillings in Yatir, Israel.

Depth (m)	Yatir 1 December 2006				Yatir 3 April 2009				Yatir 4 July 2010					
	H (%)	DIC$_{sed}$ mm/L	δ13C (‰)	δ18O (‰)	H (%)	DIC$_{sed}$ mm/L	δ13C (‰)	Δ14C (‰)	H (%)	DIC$_{sed}$ mm/L	δ13C (‰)	Δ14C (‰)	δ18O (‰)	Tritium (TU)
0.08									2.9	1.0	−14.8		1.2	
0.25	11.4	5.2	−14.6	5.5	9.9	3.2	−21.3	−139.6						
0.30									7.1	2.5	−18.7	−93.7	1.0	
0.40									10.1	3.4	−17.4		−0.7	
0.65									10.3	3.7	−16.9		−1.4	
0.75	12.1	4.8	−13.7	−0.3	8.9	3.5	−19.8	−141.8	10.8	3.2	−21.0		−2.0	
0.85									11.0	5.3	−18.0	−148.7	−2.5	
0.95									10.3	4.3	−18.1		−2.3	6.3 ± 2.7
1.05									10.0	5.2	−15.0	−189.9	−2.5	
1.15									11.9	4.0	−16.4	−145.7	−2.4	
1.25	13.2	5.3	−13.9	−1.7	10.1	3.3	−17.7	−178.1						
1.35									10.0	5.8	−16.9	−241.8	−2.6	
1.48									11.7	4.0	−16.7	−232.0	−2.7	
1.63									11.6	4.5	−14.9	−215.4	−3.2	
1.75	12.5	3.7	−10.0		10.4	3.4	−14.5	−366.4						3.7 ± 2.3
1.80									10.2	4.7	−14.6	−328.2	−3.7	
2.00									12.8	7.4	−14.6			
2.20									11.3	5.0	−13.7	−304.6	−3.5	
2.25	12.9	5.8	−11.1	−3.0	10.8	4.0	−13.3	−711.6						
2.38									13.6	4.8	−11.9	−307.6	−3.6	
2.53									14.5	4.9	−11.1		−3.4	4.3 ± 2.3
2.70									12.0	4.5	−11.5		−3.8	
2.75	12.8	6.7	−7.5	−2.7	11.1	6.3	−14.3	−402.7						
2.88									12.2	4.3	−12.0		−4.1	
3.05									11.4	3.5	−10.9	−365.4	−3.4	2.3 ± 2.3
3.23									12.3	4.3	−12.8		−3.9	
3.40									14.1	3.4	−11.4		−3.9	1.3 ± 2.3
3.58									14.2	3.4	−9.7	−377.2	−3.6	
3.73									14.8	4.8	−11.5			1.3 ± 2.3
3.90									14.9	3.8	−10.1	−436.0	−3.6	
4.15									13.4	3.4	−12.2	−494.9	−3.6	
4.35									18.8	4.9	−11.8		−4.6	

Recent input of rainwater is indicated in the topmost part of the section in April 2009 (Figure 3c and Table 1) by a slightly lighter (i.e. more negative) $\delta^{18}O$. In regional rains, the range of $\delta^{18}O$ values is about −4‰ to −5 ‰ (Gat and Dansgaard 1972). In July 2010, below 2 m depth, the $\delta^{18}O$ approaches that of regional rain and suggests infiltration of rainwater.

Tritium in the Moisture of the USZ and the Rate of Downward Flow of Water

Tritium ($t_{1/2}$ = 12.32 yr), produced in the atmosphere, is present in the rainwater that enters the USZ. Because of its short half-life, it is useful for estimating the flow of water there. Regular collection of rainwater in Israel for the measurement of tritium was stopped in 2001 and the last annual average (in 2001) was ~3 TU (1 TU = 10^{18}[T/H]), which is similar to the pre-thermonuclear level of 3.4 to 6.6 TU (Kaufmann and Libby 1954).

The results of the tritium measurements are given in Table 1 and Figure 3c. The quantity of available water was small; therefore, tritium was measured directly, without enrichment. For this reason, the standard deviations of the data are large. For several years before 2001, the tritium in winter rains in Israel was quite similar to that of 2001 (http://www.univie.ac.at/cartography/project/wiser/). The topmost value in the Yatir profile is similar to the high value cited by Kaufmann and Libby (1954), but the large associated error (σ) could make it close to their lower values. The two values below this high value are quite close to the Kaufmann and Libby (1954) low values. The three deepest values are significantly lower than 3 TU due to radioactive decay. Two of them (depths of 3.4 and 3.9 m) are identical and their average depth was used in the calculation. In this case, the decay age of tritium is calculated from $t = -17.93\ln(TU_t/TU_0)$, where t is the age, 17.93 is the average age of tritium, TU_0 is the tritium concentration of the rain, and TU_t is the tritium concentration after decay. The decay time of tritium between depths of 0.95 to 3.56 m is t = 24 yr. Thus, there is a downward flow of water through the USZ of ~0.11 m yr^{-1}. This flow is related to intensive rain events that overcome evaporation by infiltrating the USZ. In Nizzanim, Israel, the rate of movement of water in the USZ was estimated using the thermonuclear pulse of tritium in rains, which was detected in 2003 at ~18 m depth, indicating a downward flow of 0.45 m yr^{-1} (Carmi et al. 2009).

Dissolved Inorganic Carbon (DIC$_{sed}$) in the USZ

DIC in water is commonly expressed in moles of carbon in a volume of 1 L of water (moles C L^{-1}). In the USZ, the DIC will be expressed in moles C in a volume of 1 L of sediment (DIC$_{sed}$). Estimating the DIC$_{sed}$ requires taking into account the water content in this 1 L of sediment. The range of DIC$_{sed}$ in the three cores is between about 1 to 7.5 mmoles L$_{sed}^{-1}$. In the profiles of December 2006 and April 2009, high DIC$_{sed}$ values were found at depth of ~2.5 m (Table 1 and Figure 4a). To investigate the distribution of DIC$_{sed}$ in the vicinity of this depth, a deeper drilling, down to 4.5 m, was undertaken in July 2010 (Table 1 and Figure 4a). In this profile, a peak value of DIC$_{sed}$ was observed at 2 m depth and the distribution of DIC$_{sed}$ around this depth suggests diffusion from a local source, e.g. a root. The high DIC$_{sed}$ in the first two profiles at depths of 2.75 m can also be reasonably attributed to nearby roots. An estimate of the "strength of the source" of CO_2 evolved from the roots, which appear as DIC$_{sed}$ in the profile of July 2010, done using the data points (Figure 4a) around the depth of 2 m, is approximately 10.9 mmol C dm^{-2}. In the same drilling, there are also hints for weaker sources closer to the surface (0.75 m) and at ~1.10 m depth. Evidence for the activity of these sources was observed in the soil gas of Yatir (Carmi et al. 2013).

δ^{13}C (‰) in the DIC and in the Sediment of the USZ

When $CO_{2(gas)}$ in the sediment becomes bicarbonate in the DIC$_{sed}$, its δ^{13}C (‰) changes in two steps. The first step is dissolution of $CO_{2(gas)}$ into the sediment water to become $CO_{2(aq)}$, with a decrease of about 1‰ in its δ^{13}C (‰) (which becomes more negative); the second step is the conversion of $CO_{2(aq)}$ to bicarbonate, with an increase of about 9‰; that is, its δ^{13}C (‰) becomes less negative (Clark and Fritz 1997). A further step is precipitation of carbonate from the DIC$_{sed}$, carbonate which is heavier than the bicarbonate (less negative) by ~1‰ (Clark and Fritz 1997), thus leaving the residual bicarbonate slightly more depleted in δ^{13}C. Exchange of carbon between the DIC and the

sediment by precipitation/dissolution of carbonate tends to bring the $\delta^{13}C$ of the DIC towards heavier values, closer to those of the solid sediment.
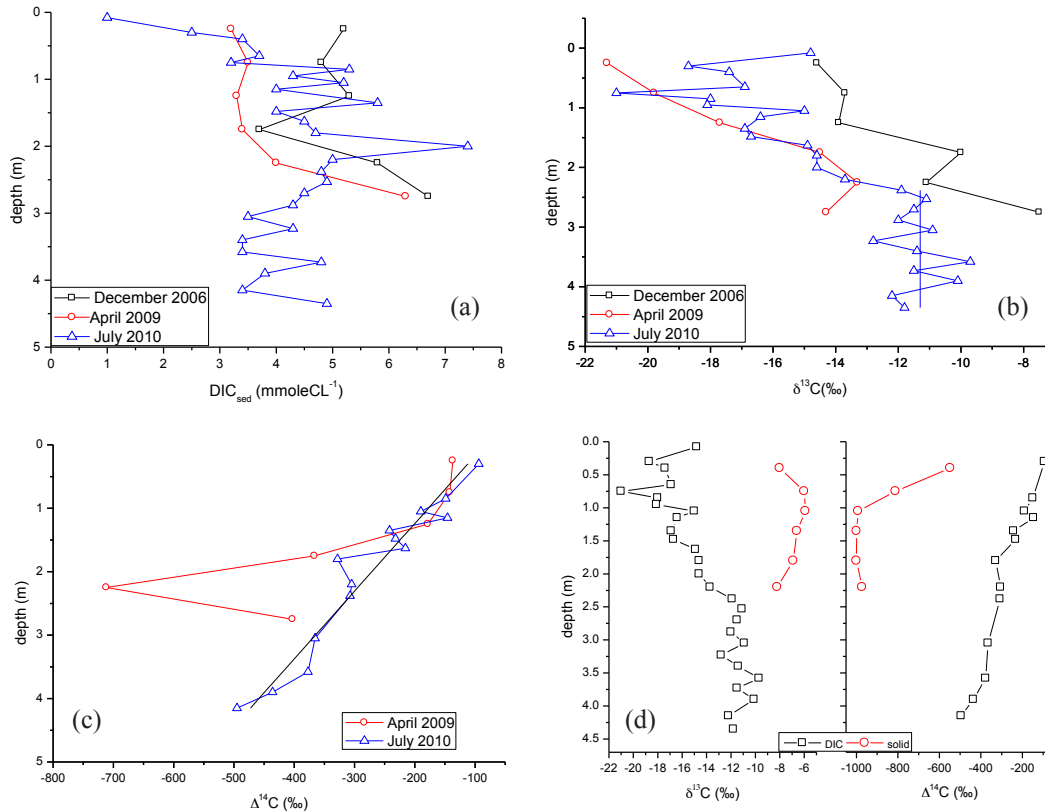

Figure 4 (a) Dissolved inorganic carbon (DIC_{sed}) (mmole Cl^{-1}) in the soil water of the sediment section in Yatir; (b) $\delta^{13}C$ (‰) in the DIC in the soil water of the sediment section in the cores of Yatir. The average below 2.5 m in July 2010 is $-11.4‰$; (c) $\Delta^{14}C$ (‰) in the DIC in the soil water of the sediment in Yatir, and the linear fit for July 2010 is $\Delta^{14}C (Z) = -93.8 \times Z - 83.8$ ($r^2 = 0.93$); (d) $\delta^{13}C$ (‰) and $\Delta^{14}C$ (‰) in the DIC and in the solid of the core of July 2010 in Yatir. The regressions are $\Delta^{14}C (Z) = -93.8 \times Z - 83.8$ for the DIC and $\Delta^{14}C_{carb} (Z) = -683.9 \times Z - 281.7$ for the top 1 m of the sediment.

The $\delta^{13}C_{DICsed}$ (‰) values are shown in Table 1 and Figure 4b. The April 2009 profile is the "cleanest" of the three profiles and is therefore used to elucidate the main diagenetic processes in the USZ. In April 2009, the $\delta^{13}C$ of the DIC_{sed} ($-21.3‰$) at the top suggests dissolution of CO_2 gas of about $-20‰$, and then a gradual change with depth, from $CO_{2(aq)}$ to bicarbonate values (Figure 4b and Table 1) down to the depth of 2.25 m to about $-14‰$. This slow rate of change is related to the activity of roots, which contribute isotopically lighter (more negative) $CO_{2(aq)}$ along the USZ, down to depth of 2.25 m.

The biological activity in the top 1 m of the section in December 2006 is low: this is also seen in the soil gas of January 2008 (Carmi et al. 2013). There is no recent input of CO_2 into the USZ and the *whole* profile has become bicarbonate. In the photograph taken in December 2006 (Figure 1b), it is seen that the plants on the surface are all dried out. When alive, these plants contribute $CO_{2(gas)}$ through their roots to the top of the USZ.

In the top of the sediment column in July 2010, there is a source of CO_2 at about 0.85 m (Table 1)

and $\delta^{13}C = -21‰$ at about 0.75 m (Table 1) that contributes $CO_{2(aq)}$ to the DIC_{sed}. Above and below this depth, the $\delta^{13}C$ values indicate mixtures of $CO_{2(aq)}$ and bicarbonate. Below 2.4 m and down to 4.4 m, the $\delta^{13}C$ is quite constant with an average of $-11.4 \pm 1.0‰$. This value compares well with the $\delta^{13}C$ of the mountain aquifer ($-12.5 \pm 0.2‰$) (Kroitoru et al. 1989), and with the DIC in the coastal aquifer ($-11.4 \pm 1.7‰$) (Bruce et al. 2007).

$\Delta^{14}C$ in the DIC_{sed} and in the Solid Sedimentary Carbonate of the USZ

The two available profiles of ^{14}C in the DIC_{sed} of the USZ of Yatir, that of April 2009 and July 2010 (Figure 4c and Table 1), are quite similar but for the data point at 2.25 m in April 2009. In both profiles, the $\Delta^{14}C$ in the DIC_{sed} decreases significantly with depth. This effect is thought to be due to chemical deposition/exchange processes between the soil water and the carbonate of the sediment as is the case of $\delta^{13}C$, which may change the values by ~1‰ (Clark and Fritz 1997). This is a change of 5–10% in the $\delta^{13}C$, which is significant and measurable. In the case of $\Delta^{14}C$, the exchange may change the values by ~2‰. This is variation of 0.2% to 2% is quite small; therefore, fractionation is not considered in the exchange between the DIC_{sed} and the sediment. The possibility that the decrease in $\Delta^{14}C$ is due to decay is ruled out because in such a case the DIC_{sed} will have to stay in the USZ for thousands of years. The resolution of the April 2009 profile is not detailed enough and will not be discussed further. For July 2010, the resolution of the data is better. At the top, at 0.3 m, the $\Delta^{14}C$ in the DIC_{sed} is closest to the $\Delta^{14}C$ of atmospheric CO_2. Below that depth, a gradient with depth is very clear. The correlation between $\Delta^{14}C$ and depth Z (in meters) is good ($r^2 = 0.93$) and the linear fit between them is $\Delta^{14}C (Z) = -93.8 \times Z - 83.8$, shown in Figure 4c. Precipitation alone does not affect the $\Delta^{14}C$ in the DIC_{sed} that remains in the liquid phase of the USZ and would therefore produce a uniform profile of $\Delta^{14}C_{DICsed}$ with depth. The decrease of $\Delta^{14}C$ with depth is therefore the result of exchange between the two phases: precipitation of carbonate labeled by $\Delta^{14}C_{DICsed}$ from the DIC and dissolution of carbonate from the sediment into the DIC, in which the ^{14}C had decayed. From the linear fit (Figure 4d), the rate of decrease (i.e. exchange) of $\Delta^{14}C$ (‰) in July 2010 is $-94‰$ m^{-1}. Using the average downward flow of water through the USZ of 0.11 myr^{-1} (calculated from the tritium data), it becomes $-10.3‰$ or -1% yr^{-1}. This rate of exchange between the $DI^{14}C$ and the sediment is quite similar to the rate of exchange for the USZ of Nizzanim in the coastal aquifer of Israel, which is 1.2% yr^{-1} (Carmi et al. 2009). The rate of carbonate precipitation in Nizzanim, derived from the decrease with depth of the DIC, was 3.2% yr^{-1}. It is inferred from the similarity between the Yatir and Nizzanim rates of exchange that the rates of precipitation of carbonate from the DIC_{sed} are also similar. Therefore, in Yatir the rate of carbonate precipitation is estimated to be 2.7% yr^{-1}.

In the top meter of the sediment, there is a good correlation between the $\Delta^{14}C_{carb}$ (‰) of the carbonate fraction and the depth Z ($r^2 = 0.998$). At 1 m depth, the $\Delta^{14}C$ is very close to $-1000‰$, i.e. it is devoid of ^{14}C, and the reason for this is discussed below. The gradient between the top of the sediment core to the 1 m depth can be written as $\Delta^{14}C_{carb} (Z) = -683.9 \times Z - 281.7$.

Precipitation of Carbonate and $^{14}C_{carb}$ from the DIC_{sed} onto the Sediment

As discussed earlier, the loss of carbon from the DIC by precipitation of carbonate on the sediment is estimated to be at a rate of 2.7% yr^{-1}. It follows that there is a carbonate precipitation of ~2 mg C L$_{sed}^{-1}$ yr^{-1}. This is a very minor contribution to the carbonate of the sediment, which is 28.2 g C L$_{sed}^{-1}$ (1 L of sediment with porosity of 53% has 47% of solid sediment; the density of the dry sediment and the calcite content are 2.5 g mL^{-1} and 20%, respectively).

For ^{14}C the transfer from the DIC_{sed} to the sediment by precipitation (2.7%) and exchange (1.0%) is at the rate of 3.7% yr^{-1}. The annual expected change of $\Delta^{14}C_{carb}$ in the sediment, at several depths,

has been calculated by mass balance from the moles of carbonate in the sediment, with the moles of carbonate deposited annually from the DIC and their respective ^{14}C concentrations. The annual radioactive decay of [14]C (0.12‰ yr⁻¹) is then subtracted from the calculated annual deposition of [14]C (0.37‰ to 1.23‰) to give the expected *net* annual change of ^{14}C in the solid sediment, which is between 0.25 and 1.1‰ yr⁻¹. This minor contribution of ^{14}C cannot be observed because it is below the limit of detection and it may explain why although there was a significant concentration of [14]C_{DIC} below 1 m depth (Figure 4d), no sedimentary ^{14}C could be detected. The presence of [14]C_{DICsed} is transient and it did not have enough time to significantly affect the sediment. However, this estimate leaves open the question of how did the ^{14}C accumulate in the topmost meter of sediment.

A possible explanation is that allogenic dust particles settling on the sediment bear [14]C. Extrapolation of the Δ[14]C_{carb} to the surface yields a value of –282‰. It is noted that in the allogenic particulates of the Jordan River entering Lake Kinneret, a similar value (–280‰) was found for the ^{14}C of the carbonate fraction (Stiller et al. 1988). The source of these allogenic particulates was attributed to dust that had been swept into the Jordan River by the rainwater. Thus, it is reasonable to assume that the source of the Δ[14]C_{carb} in the sediment of Yatir could be ^{14}C-bearing dust that had settled on the surface. The apparent age difference (excluding the effect of precipitation/exchange of ^{14}C) between the depths of 0.4 and 0.75 m (0.35 m difference) in the solid sediment of Yatir is 7200 yr, which yields a crude average estimate for sediment built up between these depths at a rate of ~0.05 mm yr⁻¹.

The rate of sediment buildup of 0.05 mm yr⁻¹ between 0.4 and 0.75 m is used to estimate the time of accumulation of dust in the upper 1.35 m, where ^{14}C was present (Figure 4d and Table 2). This time period is ~28 kyr old, so the buildup began at the very end of the Pleistocene, continuing through the Holocene until today. Assuming that the same rate of sediment buildup can be applied below the 1.35 m depth, i.e. down to the bedrock at 4.8 m, the time of accumulation for these 3.45 m is ~71 kyr. The buildup of the sediment thus began at ~100 kyr BP, suggesting that it is from the last stage of the Pleistocene. The absence of ^{14}C in the lower part of the sediment is due to decay, for which there was ample time.

Table 2 Carbon isotopes in the solid carbonate of the sediment in Yatir, Israel.

Depth (m)	δ^{13}C (‰)	Δ^{14}C (‰)
0.40	–8.0	–547.9
0.75	–6.0	–810.7
1.05	–5.9	–991.2
1.35	–6.6	–999.0
1.80	–6.9	–999.8
2.20	–8.2	–972.1

SUMMARY AND CONCLUSION

The present work together with the previous one on the soil gas (Carmi et al. 2013) provide a comprehensive study of the carbon system in the USZ of the semi-arid site of Yatir. The three detailed cores that were collected in three different seasons offered insight into the physical and chemical processes taking place in the USZ of Yatir. The mineralogical composition of the USZ of Yatir can be regarded as quite uniform (Figure 3a). Accumulation of water at depth and evaporation at the top of the USZ were inferred from the moisture and the [18]O data. The rate of flow in the USZ was estimated from the tritium data. The profiles of DIC and ^{13}C show that at the top, down to a depth of about 1 m, seasonal plants contribute CO_2 to the system. At mid-depths down to approximately

2 m, the profiles show that roots of forest trees planted in the 1960s contributed CO_2 to the USZ. At depths deeper than ~2.7 m, no emanation of CO_2 from roots was observed. From the profile of ^{14}C in the DIC, the rate of exchange between the porewater and the sediment was estimated. The rate of precipitation of carbonate from the DIC to the sediment is very small compared to the sediment carbonate content. The absence of ^{14}C in the deep sediment is explained by the very small net rate of deposition of ^{14}C from the DIC$_{sed}$ to the sediment, which cannot be detected on an annual basis. A possible explanation for the presence of ^{14}C in the top solid sediment is sedimentation of dust tagged by ^{14}C. The rate of accumulation of dust was calculated using the ^{14}C data at the upper part of the sediment (0.05 mm yr^{-1}). The time for accumulation of the sediment column from the bedrock to the surface was estimated to be about 100 kyr.

By comparing the processes in the USZ to that of a higher rainfall (400 mm yr^{-1}) region in Nizzanim (Carmi et al. 2009) and the lower rainfall in Yatir (280 mm yr^{-1}), it is seen that the rate of downward movement of water in Nizzanim (0.45 m yr^{-1}) is faster than that of Yatir (0.11 m yr^{-1}). The rates of exchange of carbon between the DIC$_{sed}$ and the solid sediment were found to be similar at both sites. In Nizzanim, the ^{13}C value of the coastal aquifer is reached close to the exit from the USZ into the aquifer, at 20 m depth, whereas in Yatir the ^{13}C value of the mountain aquifer of Israel is reached at the depth of 2.5 m.

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