VARIATIONS IN SOIL CO₂ CONCENTRATIONS AND ISOTOPIC VALUES IN A SEMI-ARID REGION DUE TO BIOTIC AND ABIOTIC PROCESSES IN THE UNSATURATED ZONE¹

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ABSTRACT. A study of CO₂ in soil gas was conducted in a bare plot in the unsaturated zone (USZ) of Yatir Forest, northern Negev, Israel. In 2006, 6 tubes for sampling of soil gas were inserted into the USZ to depths of 30, 60, 90, 120, 200, and 240 cm. Profiles of soil gas in the USZ were collected from the tubes 5 times between October 2007 and September 2008. Measurements of the collected profiles of soil gas were of CO₂ (ppm), δ₁³C (‰), and Δ¹⁴C (‰). At all times, the concentration of CO₂ in the soil gas was higher than in the air at the surface (CO₂ ~ 400 ppm; δ₁³C ~ –9‰). The main source of the CO₂ in soil gas is from biotic activity released through roots of trees and of seasonal plants close to the surface. In the winter, the CO₂ concentrations were lowest (6000 ppm) and the δ₁³C was –20‰. In the spring and through the summer, the CO₂ concentration increased. It was estimated that the major source of CO₂ is at ~240 cm depth (δ₁³C ~ –22‰; CO₂ ~ 9000 ppm) or below. Above this level, the concentrations decrease and the δ₁³C (‰) become more positive. The ¹⁴C values in the measured profile are all less than atmospheric and biotic ¹⁴C. It was deduced that biotic CO₂ dissolves in porewater to form carbonic acid, which then dissolves secondary carbonate (δ₁³C ~ –8‰; ¹⁴C ~ –900‰) from the sediments of the USZ. With the ¹⁴C data, the subsequent release of CO₂ into the soil gas was then estimated. The ¹⁴C data, supported by the ¹³C and CO₂ data, also indicate a biotic source at the root zone, at about 90 cm depth.

INTRODUCTION

CO₂ from the unsaturated zone (USZ) is considered to play a significant role in the balance of this gas in the atmosphere. Therefore, a significant effort has been expended in determining the concentration and isotopic composition of CO₂ in the USZ and in understanding the effect that it has on the atmosphere. Most of the work done was by collecting the respired CO₂ in an isolated volume above the USZ. Davidson (1995) estimated that the δ₁³C (‰) of the CO₂ in the soil gas came mostly from C₃ sources.

Parker et al. (1983) studied the respiration of CO₂ above grassland in Texas and estimated the flux of CO₂ out of the USZ and the rate of mineralization in the USZ. Gorzyca et al. (these proceedings) studied soil-respired CO₂ and its isotopes for 7 yr in several ecosystems in southern Poland by collection of CO₂ above the USZ. They measured the carbon isotopes and found a dependence on industrialization in the vicinity of their sampling sites.

In the USZ, Pumpanen et al. (2008) installed permanent probes in the USZ to collect data on the profile of CO₂ concentrations in the USZ in spring time. They applied diffusion to calculate the efflux from the soil to the atmosphere for that time. Liu et al. (2006) used CO₂ mass balance and δ¹³C to calculate the proportions of CO₂ from decomposed organic matter and from air in the soil gas of a boreal forest. They studied the transport of CO₂ in soil gas with ¹⁴C. The contribution of CO₂ from carbonate mineral in the USZ is considered to be significant. According to Deines et al. (1974), dissolution of carbonate minerals in the USZ is regulated by acidity and pCO₂, with higher pCO₂ resulting in greater amounts of carbonate dissolution.

¹This paper is dedicated to the memory of Prof JR Gat (1926–2012), mentor and a good friend.
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The purpose of this study was to understand processes in the USZ in a bare plot, the various sources of CO₂ therein, and the mode of its transfer to and from the atmosphere. For this purpose, a matrix of 5 profiles of CO₂ and δ¹³CO₂ was obtained over 1 yr (October 2007 to September 2008). ¹⁴C was measured in the profile of May 2008.

SITE DESCRIPTION

The Yatir Forest (31°20′N, 35°03′E, 650 m asl) is located in a semi-arid zone (290 mm/yr rain) on the southwestern flanks of the Judea Mountains of Israel (Figure 1a). The forest was planted by the Jewish National Fund in the 1960s and it is the site of the Yatir bio-ecological station of the Weizmann Institute of Science, which was erected in spring 2000 (Grünzweig et al. 2003). Among the many studies done at that station are those of CO₂ efflux from the USZ with diurnal resolution, reported by Maseyk et al. (2008) and Grünzweig et al. (2009). The site of the present study of soil gas CO₂ is a bare 20 × 20 m plot in the forest, 100 m to the east of the Yatir bio-ecological station.

METHODS

In December 2006, 6 holes were drilled into the USZ of a bare plot in the Yatir Forest (Figure 1b) for the collection of soil gas. The holes were drilled to depths of 30, 60, 90, 120, 200, and 240 cm. PVC tubes (18 mm diameter) were inserted into the holes and left open at both ends: one in the USZ to the specified depth, and the other to the atmosphere. The system was left to settle for 10 months before the sampling began. Between the samplings, the local fauna sometimes gnawed the tops of
the sampling tubes, but, when this happened, the problems were overcome successfully. After the
third sampling, the 90-cm-deep tube became blocked and could not be further sampled.

Two methods of sampling were used and gave similar results. In the first method (Carmi 2007), cal-
ibrated glass vessels fitted with valves were pre-evacuated in the lab at the Kimmel Center for
Archaeological Research of the Weizmann Institute of Science, and then connected to the tubes in
the field. The valves were then opened and the pressure in them was monitored. In the USZ, the
pressure of soil gas is atmospheric. Following several minutes for equilibration, the valves were
closed. In the lab, the vessels were connected to a vacuum line, the volume of soil gas was measured,
and the CO₂ was separated from the soil gas. The volume of CO₂ was then measured and its concen-
tration (ppm) was calculated (Carmi 2007). The CO₂ was saved for further measurements. ¹³C was
measured in a Finnigan Mat 250 mass spectrometer in the Department of Environmental Science
and Energy Research at the Weizmann Institute of Science. ¹⁴C was measured in the profile of May
2008 by the NSF-Arizona AMS laboratory. In the second method of sampling, vessels with 2 valves
were brought to the field, connected to the tubes, flushed 8–10 times by pumping soil gas through
them after which the valves were closed. In the lab, the vessels were connected directly to a Carlo
Erba 1108 elemental analyzer coupled to a continuous-flow Micromass isotope ratio spectrometer,
for measurement of the concentrations of CO₂ (ppm) and δ¹³C (‰) (Klein et al. 2005). In this
method, the samples were small and ¹⁴C was not measured.

RESULTS AND DISCUSSION

The results of the 5 samplings at 6 depths in the USZ of the bare plot near the Yatir forest are given
in Table 1. The data are presented graphically in 2 ways: as depth profiles at the time of sampling
(Figures 2a,b and c) as well as chronologically for each depth (Figure 3a,b).

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Depth Profiles of CO₂ and Its Isotopes

The concentration of CO₂ (ppm) in the soil gas of Yatir (Figure 2a and Table 1) is always highest at
the 240 cm depth, suggesting a nearby source. From 240 cm upwards towards the surface, CO₂ gen-
erally decreases. There are a few exceptions to this trend, such as in August and September 2008
when there was, near the surface (at ~30 cm depth), an increase in the CO₂ concentration relative to
earlier profiles. At the root zone, 90 cm deep, an apparent increase in the CO₂ concentration is
observed in May 2008.

The most negative values of δ¹³C at the bottom of the profiles (August and September 2008) are
quite similar to those of C₃ plants. This suggests that the sources are roots of C₃ plants in the near
vicinity (Figure 2b and Table 1). The δ¹³C values become more positive towards the top of the USZ.
The most positive δ¹³C is observed at the top of the section in January 2008. The low CO₂ and the
more positive $\delta^{13}C$ of January 2008 at the top of the profile suggest an input from the atmosphere above (400 ppm and $-9\%$). At the end of the summer, the increased concentration of CO$_2$ at the top of the section together with the slightly more negative $\delta^{13}C$ suggests contribution from seasonal plants. The dry remains of seasonal plants are seen on the surface in December (Figure 1b).

The profiles of CO$_2$, $\delta^{13}C$ ($\%$), and $\Delta^{14}C$ ($\%$) in May 2008 are shown in Figure 2c and Table 1. The maximum in the $\Delta^{14}C$ (%) profile is at 90 cm depth. Taken together with the CO$_2$ and $\delta^{13}C$ data, the $\Delta^{14}C$ (%) clearly suggests a local biotic source of CO$_2$ well within the root zone. The $\Delta^{14}C$ (%) values in the profile are all less than the measured atmospheric values of 49.5$\%$ in 2008 (Levin et al. 2010) and less than the $\Delta^{14}C$ in the biosphere, which is assumed to be similar to the atmospheric $\Delta^{14}C$. The overall low $\Delta^{14}C$ in the soil gas CO$_2$ requires a contribution from an additional source with a low $^{14}C$ concentration.
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Seasonal Variations of CO₂ and δ¹³C

An annual cycle in the CO₂ concentrations is quite clearly manifested. In the fall and winter, the concentrations of CO₂ (ppm) decrease at all depths (Figure 3a and Table 1). This is probably due to reduced production of CO₂ by the deep source. However, at the top of the section (30 cm), the rate of decrease is smaller due to production of CO₂ in the seasonal sources at the top and at the 90-cm-deep source. In the spring and summer, the concentrations increase at all depths, at a rather similar rate. Towards the fall (September 2008), the concentrations decrease again towards dormancy.

![Figure 3](image-url) Seasonal variations of Yatir soil gas at different depths: (a, top) CO₂ (ppm); (b, bottom) δ¹³C (‰).

The δ¹³C (Figure 3b) at all depths and along the annual cycle seems to converge near −16 to −18‰. There are 2 noteworthy exceptions: one occurs at the top in January 2008, which displays the least negative value and is closest to that of the air above the USZ (as discussed above). The other exception is at 240 cm depth where the δ¹³C is always more negative and thus closest to that of C₃ plants.
Sources of CO₂ in the Soil Gas

Three biotic sources are suggested by the data at 2 depths in the May 2008 profile (90 and 240 cm perennial roots and seasonal plant roots at the top) and 1 abiotic source (air present in the soil gas of the USZ). However, as shown in Figure 2c, the Δ¹⁴C in the soil gas CO₂ (−102‰ to −248‰, Table 1) is less than the atmospheric and biosphere level of 49.5‰ in 2008 (Levin et al. 2010) (Table 1 and Figure 2c). These Δ¹⁴C (‰) values require an additional (fifth) source that contributes CO₂ with low ¹⁴C to the soil gas. The likeliest candidate for this source is the carbonate in the sediments of Yatir, a second abiotic source of CO₂ in the soil gas. Δ¹⁴C measured in the carbonate of the sediments of Yatir was found to be −899‰ to −986‰ (Table 2), while the associated δ¹³CO₂ was −8‰. Deines et al. (1974) have shown that in the presence of water and high concentrations of CO₂, dissolution of sediments can occur and contribute CO₂ to the soil gas. Assuming this to be the case at Yatir, this dissolution was estimated for May 2008 at 2 depths in the profile (90 and 200 cm). The following rough approximation was used:

\[
\Delta^{14}C \times C = \Delta^{14}C_s \times C_s + \Delta^{14}C_a \times (C_b + C_a)
\]

and

\[
C = C_s + C_b + C_a
\]

The first equation describes the mass balance for ¹⁴CO₂. The subscripts s, b, and a are, respectively, the sediment, biosphere, and atmosphere. C is the total concentration of CO₂ in soil gas and C_s, C_b, and C_a are the respective CO₂ contributions from abiotic and biotic sources in the sediment and from atmospheric origin. \(\Delta^{14}C_a = \Delta^{14}C_b = 49.5\)‰ is the assumed value for the CO₂ in the atmosphere and the biosphere. The second equation is the mass balance for CO₂. The results of the calculations for 2 levels in the USZ are shown in Table 3 and Figure 4. It is evident that the contribution from the sediment, \(C_s\), is significant, in the range of 16–22% and it is believed that this may represent the profile as a whole.

Table 2 Sources of CO₂ in the soil gas of the USZ of Yatir in May 2008 calculated using Equations 1 and 2 (see above). In every cell of the table, the first line is the actual data and the second line (in italics) is the same data in percent (%). (s = sediment; b = biosphere; a = air).

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>(C_i) (ppm)</th>
<th>(\Delta^{14}C_i) (%)</th>
<th>(C^s_i) (ppm)</th>
<th>(\Delta^{14}C^s_i) (%)</th>
<th>(C^b_i) (ppm)</th>
<th>(\Delta^{14}C^b_i) (%)</th>
<th>(C^a_i) (ppm)</th>
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<td>3399</td>
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<td>400</td>
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</tr>
</tbody>
</table>

1Measured data.  
2Results of calculations.  
3Assumed.

In principle, the δ¹³C values could be used for a similar estimate of the contribution of CO₂ by dissolution from the sediment. However, unlike the ¹⁴C values in soil gas CO₂ and in CO₂ evolved from sedimentary carbonate, which are very different (Table 2), the respective δ¹³C values are very close. The sedimentary carbonate has a δ¹³C = −8.0‰; following Clark and Fritz (1997), the δ¹³C of the released CO₂ would be −17.2‰. The soil gas CO₂ ranges between −14.8 and −17.8‰ and the atmospheric and biotic values are also not very different. Therefore, the difference in the δ¹³C values is too small to provide a reasonable estimate for the sedimentary contribution.
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Correlations Between CO₂ and δ¹³C

Figures 5a–e show the correlations between CO₂ (ppm) and δ¹³C (‰) for the 5 profiles of soil gas in Yatir. The correlation in October (Figure 5a) seems quite good and suggests a dependence between the 2 variables: δ¹³C (‰) more negative with higher concentration of CO₂ and vice versa. In January (Figure 5b), the dependence is much less pronounced, but the excursion towards less negative δ¹³C (‰) at the top again suggests influx from the air above the USZ. Not much can be said about the correlation in May (Figure 5c) because the CO₂ data is incomplete (Table 1).

The correlations in August (Figure 5d) and September (Figure 5e) are good ($R^2 = 0.99$ and 0.91, respectively) and the relations that describe them are

$$\delta^{13}C (‰) = -0.0006 \times CO₂ - 14.77$$  \hspace{1cm} (3)

and

$$\delta^{13}C (‰) = -0.0004 \times CO₂ - 17.03$$  \hspace{1cm} (4)

Extrapolations to the atmosphere (400 ppm CO₂) give δ¹³C = −15‰ in August and δ¹³C = −17.2‰ in September. However, the 2 values are significantly more negative than the atmospheric value of δ¹³C = −9‰, implying that there is a significant flow of CO₂ from the USZ to the atmosphere in these months (see below).

Fluxes of CO₂ Through the Interface Between the USZ and the Atmosphere

The data presented suggest that transport of CO₂ by diffusion is an important process in the USZ. Indeed, outflow from the USZ to the atmosphere by diffusion has been suggested by Cerling (1984). Influx of CO₂ from the atmosphere into the USZ, characterized by a lower concentration of CO₂ and less negative δ¹³C (400 ppm and −9‰, respectively) is responsible for the gradual dilution of the concentration of CO₂ in the USZ, a larger dilution at the top decreasing downward (Figure 2a). This is most evident in January 2008 (Figure 2b). It is possible to estimate the flux using the Fick equation:

$$F = -r \frac{dC}{dz}$$  \hspace{1cm} (5)
where $F$ is the flux of CO$_2$ in g C m$^{-2}$ month$^{-1}$, $C$ is the concentration of CO$_2$ (g CO$_2$ m$^{-3}$), $z$ is the depth in m, and $r$ is the effective diffusion coefficient:

$$r = D \times p \times t$$  \hspace{1cm} (6)

where $D$ is the diffusion coefficient of CO$_2$ in air (37.9 m$^2$ month$^{-1}$), $p$ is the porosity (0.51), and $t$ is the tortuosity (0.6) (Cerling 1984). For the site of Yatir, $r = 11.6$ m$^2$ month$^{-1}$. Since both the outflux and influx proceed simultaneously, the result of the calculation will be a net flux.

Figure 6 shows the calculated monthly net outfluxes of CO$_2$ from the USZ at the Yatir bare plot calculated by the Fick equation. Data between the months of May and September is not available and thus was estimated by interpolation. The resulting integrated annual outflux is 260 g C m$^{-2}$ yr$^{-1}$. It
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is, in fact, the balance between the fluxes of soil CO$_2$ from the USZ to the atmosphere and of atmospheric CO$_2$ to the USZ. This value from the bare plot can be compared to the annual flux in the Yatir Forest itself, with its 300 trees per hectare, which is 406 g C m$^{-2}$ yr$^{-1}$ (Maseyk et al. 2008) (Figure 7a). The source of CO$_2$ in the USZ is predominantly emanation from underground roots. There are no trees in the bare plot of the present study (Figure 1b); therefore, the density of the roots is low. Emanation of CO$_2$ is therefore slower and the flux out of the USZ is smaller.

![Figure 6 Calculated monthly fluxes of CO$_2$ (g C m$^{-2}$ month$^{-1}$) from the USZ to the atmosphere in Yatir. The dashed line is an interpolation.](image)

It is of interest to compare the monthly fluxes from the USZ in the Yatir bare plot with plots bare of trees in the more fertile Coastal Plain of Israel (Figure 1a, Table 3, Figure 7b). Here, the porosity is lower (0.35 compared to 0.51 in Yatir) because the proportion of clay in the sediments is much higher than in Yatir. The effective diffusion coefficient $r = 7.9$ m$^2$ month$^{-1}$ is thus significantly smaller than at Yatir. However, due to the higher productivity at Nizzanim, and despite the smaller effective diffusion coefficient, the outflux from the bare area of Nizzanim is higher than from the Yatir bare plot, both in winter and in spring (Figure 7b). It is worth noting that the relative increase between the 2 seasons is similar at both sites. In a second bare plot of the Coastal Plain, at the site of the Meteorological Service of Israel at Bet Dagan, the outflux in the spring is less than at the other 2 sites. This smaller outflux of CO$_2$ seems reasonable because it has been measured next to the meteorological monitoring instruments that are located in a plot of ground that is intentionally kept devoid of vegetation.

Table 3 Comparison of monthly CO$_2$ outfluxes in 3 sites in Israel calculated from data in Carmi et al. (2009) and Carmi (2007).

<table>
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<th>Site</th>
<th>Month</th>
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CONCLUSIONS

The sampling strategy used in this study was, of necessity, snapshots at discreet times. Yet, the methodology used in this study for measuring the soil CO₂ profiles in the USZ of the bare plot in Yatir garnered several results and conclusions. The sources of CO₂ in the soil gas could be identified as biotic activity of major, minor, and temporary roots of plants, as abiotic dissolution, and atmospheric air. The soil CO₂ is very dynamic, with annual cycles of biotic activity shown by similar seasonal variations in all depths. The outward diffusive fluxes of CO₂ are seasonally variable and are smaller in bare plots than in productive ones. During low biotic productivity (January 2008), 13C provided evidence for the flux of CO₂ from the atmosphere into the USZ.

REFERENCES

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