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Carbon dioxide efflux and pCO_2 in soils of three *Quercus ilex* montane forests

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Abstract. Soil CO_2 efflux and pCO_2 in the soil atmosphere were measured during one year at three montane sites of Mediterranean sclerophyllous forests in NE Spain. Two sites were located in the upper and lower slopes of a small catchment in the Prades mountains (mean precipitation 550 mm $year^{-1}$), and a third site was located on a lower slope in the Montseny mountains (mean precipitation 900 mm $year^{-1}$). The three sites were similar in bedrock and vegetation, but differed in soil characteristics and water availability. Seasonal variation of CO_2 efflux and soil pCO_2 were affected by soil temperature and, to a lesser extent, by soil moisture. Annual mean soil CO_2 efflux (considered as soil respiration) was similar at Montseny and at the comparably located site at Prades (83 ± 18 S.E. vs. 75 ± 9 mg CO_2 m^{-2} $hour^{-1}$, respectively), and was highest at the Prades upper slope site (122 ± 22 mg CO_2 m^{-2} $hour^{-1}$). Despite those relatively similar CO_2 effluxes, mean soil pCO_2 was much higher at both Prades sites than at Montseny. Soil pCO_2 always increased with depth at Prades while maxima pCO_2 at Montseny were often at 20–30 cm depth. A model based on gas diffusion theory was able to explain why soil pCO_2 was much higher at Prades than at Montseny, and to reproduce the shape of the vertical profile of pCO_2 at the Prades soils. Nevertheless, the model failed to simulate the soil pCO_2 maximum found at 20–30 cm depth at the Montseny site. Model simulations using a time-variable CO_2 production rate suggested that pCO_2 maxima at intermediate depth could be the result of a transient situation instead of an equilibrium one.

Key words: carbon cycle, carbon dioxide, mediterranean ecosystems, soil atmosphere, soil respiration.

Introduction

Carbon dioxide is produced in soils by the respiration of soil organisms, mainly plant roots and microorganisms. This production increases the pCO_2 of the soil atmosphere and creates a pCO_2 gradient between the soil and the external atmosphere. As a consequence, a net flux of CO_2 is established from the soil to the external atmosphere (CO_2 efflux). Carbon dioxide efflux is a measure of the biological activity of the belowground part of the ecosystem, and it has been studied mainly from an ecological or agronomical perspective (Brown & McFayden 1969; Chapman 1979; Ewel et al. 1987a, 1987b; Oberbauer et al. 1992; Witkamp 1969; see also the reviews by Raich & Schlesinger 1992 and Singh & Gupta 1977).

Part of the CO_2 produced in the soil dissolves in soil water and groundwater and, despite the lower magnitude of this flux compared to CO_2 efflux, it has a major influence on water chemistry. In addition, soil atmosphere CO_2 drives carbonic acid weathering of silicate and carbonate minerals. Hence, soil pCO_2 has been studied mainly from a geochemical and hydrochemical perspective (Atkinson 1977; Castelle & Galloway 1990; Fernandez & Kosian 1987; Parada et al. 1983; Reardon et al. 1979; Rightmire 1978). Several mechanistic models of the regulation of streamwater acidity have been developed to understand and predict the effects of acid deposition on terrestrial and aquatic ecosystems (Cosby et al. 1985; Gherini et al. 1985; Rustad et al. 1986). Soil pCO_2 has not been actually measured in the soils of most of the catchments where these models have been applied, despite the results obtained by Neal and Whitehead (1988) showing that soil pCO_2 greatly affects the simulation results obtained with one of those models (MAGIC: Cosby et al. 1985).

The purpose of this contribution is to analyse the annual cycle of soil pCO_2 and CO_2 efflux and their dependence on soil temperature and moisture in Mediterranean forests. A model based on the standard gas diffussion theory is used to better understand the relationship between vertical pCO_2 distribution and total CO_2 production.

Study sites

The mountains of Prades (41°13′ N, 0°55′ E) and Montseny (41°46′ N, 2°21′ E) belong to the Catalan precoastal range. At Prades, two sampling sites were selected within a gauged catchment (L'Avic, 51.6 ha): one in an upper slope position (975 m elevation) and the other in a lower slope position (700 m elevation). At Montseny one sampling site was selected within a permanent plot located in a lower slope position at an elevation of 670 m.

The vegetation of all three sites is closed *Quercus ilex* forest, which was coppiced until some 40 years ago and has remained undisturbed since. At the Montseny and Prades upper-slope sites there is almost no understory; at the Prades lower-slope site the understory is better developed and consists mainly of *Arbutus unedo*, *Rhamnus alaternus*, *Phyllirea latifolia* ssp. *media*, and *Viburnum tinus*. Aboveground net primary production at the Montseny site is 6.4 t ha^{-1} $year^{-1}$ (Mayor, 1990) and at Prades (mean value of the entire catchment) it is 6.1 t ha^{-1} $year^{-1}$ (Lledó, 1990).

The climate of both locations is Mediterranean with moderate precipitation, summer drought and relatively warm temperatures. Prades receives less precipitation (mean 547 mm $year^{-1}$ during the period 1981–1988) than Montseny (mean 902 mm $year^{-1}$ during the period 1983–1991) and has a more pronounced summer drought.

The three sampling sites have colluvial, stony soils on steep slopes underlain by Paleozoic phyllites. The organic horizons are 1–3 cm deep. There is a well developed A horizon, 15–40 cm deep, that gradually changes to a Bw cambic horizon (15–35 cm thick). Bedrock is found at a depth of 35–120 cm. The soils are classified as Xerochrepts in association with Xerorthents, where the cambic horizon is absent. Soil subgroup differs between sampling sites: lithic at Prades upper slope, typic at Prades lower slope, and dystric at Montseny.

Methods

Soil pCO_2, CO_2, efflux, and soil temperature and moisture were measured fortnightly at each site. The Montseny site was normally visited the day after the Prades sites. At the Prades upper slope site, two sampling dates were missed because of a deep snow cover. Results are reported for the period from 22 May 1991 to 20 May 1992.

pCO_2 in the soil atmosphere

At each sampling site, three sets of six permanent tubes of stainless steel (1.5 mm internal diameter) were installed at depths of 10, 20, 30, 40, 50, and 75 cm. The upper part of the tubes was capped with a rubber septum suitable for gas sampling with plastic syringes. Before sampling, 10 mL of soil air were withdrawn from each tube and discarded. A second 8-mL volume was then withdrawn and injected into a 5.5 mL evacuated Vacutainer, thus ensuring a positive pressure within the Vacutainer to avoid inward gas flow during transportation. On several sampling dates, a third 8-mL volume was withdrawn from the same tube and no differences in CO_2 concentration were detected between the second and the third 8 mL samples. While the Vacutainers were pre-evacuated by the manufacturer (Beckton & Dickinson), the residual atmosphere contained enough CO_2 to contaminate the samples (plus at least three other unidentified gases detectable with a flame GC detector). To overcome this contamination the Vacutainers were opened, allowed to equilibrate with the open atmosphere for several hours, capped again with the original rubber caps, and then re-evacuated in a vacuum line. Several tests using standard gases were conducted to establish the extent of the CO_2 contamination due to the residual gas contained in the re-evacuated Vacutainers. The maximum error attributable to the re-evacuation procedure was a 5% overestimation of pCO_2 at 425 $\mu L\ L^{-1}$, and a 5% underestimation of pCO_2 at 10100 $\mu L\ L^{-1}$. Tests were made in order to indicate how long the Vacutainers held sample;

the observed loss 48 hours after filling them with an standard gas was 3%. No corrections were applied to the actually measured pCO_2.

pCO_2 of samples contained in Vacutainers was measured by injecting 0.5 mL directly into a gas chromatograph (Hewlett Packard 5890 Series II). CO_2 was separated from other gases in a Porapaq QS column, and was quantified using a thermal conductivity detector. Carrier gas was H_2. Certified standards (425 $\mu L\ L^{-1}$ and 10100 $\mu L\ L^{-1}$) were run each 6–9 samples. Analyses were always conducted within 36 hours of sampling, and usually during the same day.

CO_2 efflux

Soil CO_2 efflux was measured *in situ* using a flow-through chamber method and an infrared gas analyzer system (IRGA; model LCA-2 of ADC, Hoddesdon, Herts., England). Five permanent metal frames (20 ×20 cm^2) were inserted 3 cm into the mineral soil at each sampling site and these served as chamber supports. These frames allowed litterfall inputs to the soil and free exchange of air and water between the soil and the atmosphere. At the time of measurement (normally between 10 a.m. and 2 p.m.), the frames were capped with a measuring chamber (1.5 L volume) similar to that described by Rolston (1986). Air was sucked from the chamber at a rate of 400 mL min^{-1} with the air supply unit ASU(MF) of the IRGA system. The chamber contained enough holes to avoid a negative pressure within the chamber and prevent the mass flow of soil air to the chamber, but no measurements were made of the differential pressure between the chamber and the surrounding atmosphere. Measurements at each single chamber took 16 minutes. The first 8 minutes were allowed for equilibration of CO_2 concentrations in the effluent stream, and the mean CO_2 concentration during the last 8 minutes was used for CO_2 efflux calculations. Every 30 s, pCO_2 at the outlet of the chamber was measured in the analysis channel of the IRGA, and the pCO_2 of the surrounding air in the reference channel. By knowing the surface of the chamber (A: m^2), the air pumping rate (v: m^3 air $hour^{-1}$), and the difference of pCO_2 between the analysis and the reference channels (δ: mg CO_2 m^{-3} air), soil CO_2 efflux (F: mg CO_2 m^{-2} $hour^{-1}$) was computed in the following way (Rolston 1986):

$$F = \delta \cdot v/A$$

Results of CO_2 efflux were corrected for the mean atmospheric pressure at the sampling site (according to the elevation above the sea level) and for air temperature at sampling time.

Table 1. pH, organic carbon and total nitrogen of the Montseny and Prades soils. Soil samples corresponding to individual horizons were grouped at each site into A and B soil horizons (n is the number of individual soil samples that were classified as A and B horizons in the three soil profiles excavated at each site).

	Montseny		Prades			
			Upper slope		Lower slope	
Horizon	A	B	A	B	A	B
n	5	8	7	3	5	8
pH water	5.68	5.41	6.05	5.37	7.28	6.84
pH KCl	4.69	4.22	4.93	3.73	6.33	5.21
C_{org} (%)	3.92	1.68	3.45	0.86	4.18	0.81
N_{total} (%)	0.29	0.16	0.22	0.08	0.30	0.10

Soil temperature and moisture

Soil temperature was measured at 10- cm depth by inserting into the soil a thermistor probe in five replicate points adjacent to chamber positions at the time of CO_2 sampling. For soil moisture, three replicates of the upper 20 cm of the soil were taken for each sampling date at each site. Soil moisture was determined gravimetrically by drying the soil at 105 °C for 24 hours, and is expressed as percent weight of dry sieved (<2 mm) soil.

Physical and chemical characterization of soils

After the end of the measurement period of pCO_2 and CO_2 efflux, three pits were dug in each of the three studied sites. Soil was excavated down to the bedrock (Prades upper slope) or to around 100 cm if the soil-bedrock interface was deeper (Prades lower slope and Montseny). Soil samples were taken according to the *in situ* definition of soil horizons. Intact soil cylinders were taken in each horizon when the stoniness allowed it in order to measure bulk densities. Once in the lab, soil samples were air dried, sieved through a 2-mm mesh, and analyzed for pH (with water and with KCl), total organic carbon, total nitrogen and texture (ISSS textural classes). Total porosity (f) was calculated from measured bulk density (ρ_b) according to the expression:

$$f = 1 - (\rho_b/\rho_r)$$

where ρ_r is the mean density of particles in the mineral soil (assumed to be 2.65 g cm^{-3}).

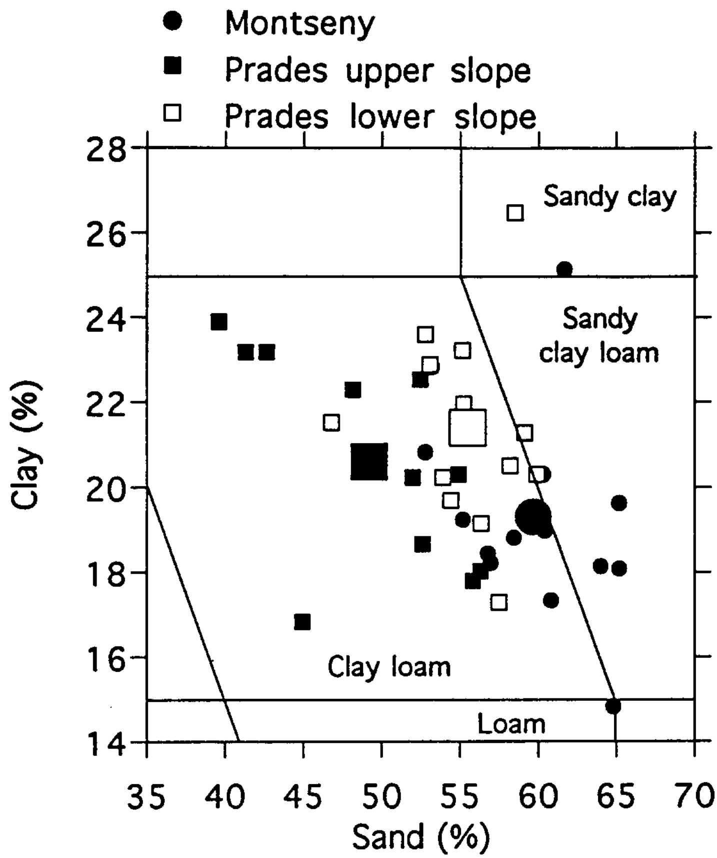

Fig. 1. Texture diagram of the soils at Prades and Montseny. Textural classes were defined according the ISSS standard. The three large symbols correspond to the arithmetic mean of each site.

Table 2. Mean values of some physical characteristics of the Montseny and Prades soils. Each value is the mean of three soil profiles excavated at each site. In brackets the standard deviation.

	Montseny	Prades upper slope	Prades lower slope
Bulk density (g cm^{-3})	1.43 (0.02)	1.26 (0.09)	1.32 (0.03)
Total porosity (cm^3 cm^{-3})	0.46 (0.01)	0.52 (0.03)	0.50 (0.02)
Stoniness (%)	69 (5.1)	64 (11)	62 (3.6)
Depth (cm)	80 (9)	48 (13)	102 (18)

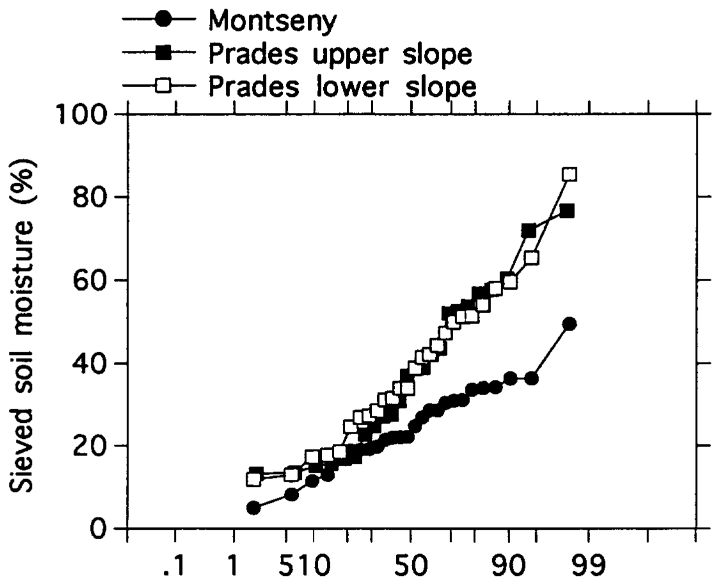

Fig. 2. Cumulative probability plot of the gravimetric soil moisture of the 2-mm sieved soil at Prades and Montseny during the sampling period.

Mean bulk density, total porosity, and stoniness (coarse particle >2 mm, mostly coarse gravels and stones) of each soil profile were calculated as the mean of bulk, total porosity, and stoniness of each horizon weighted by its corresponding depth.

Results

Soil characteristics

Soils were moderately acidic at Montseny and at Prades upper slope and neutral at Prades lower slope (Table 1). Almost all soil samples had a clay loam texture, but the Montseny soil was richer in sand and poorer in silt and clay (Fig. 1). This textural difference seems to play an important role in explaining the observed values of soil water content and soil pCO_2 at Prades and Montseny. Bulk density was higher and porosity lower at Montseny than at Prades (Table 2). As the bulk density tended to increase with depth, and soil was shallower at Prades upper slope than at Prades lower slope, mean bulk density was slightly lower in the former site.

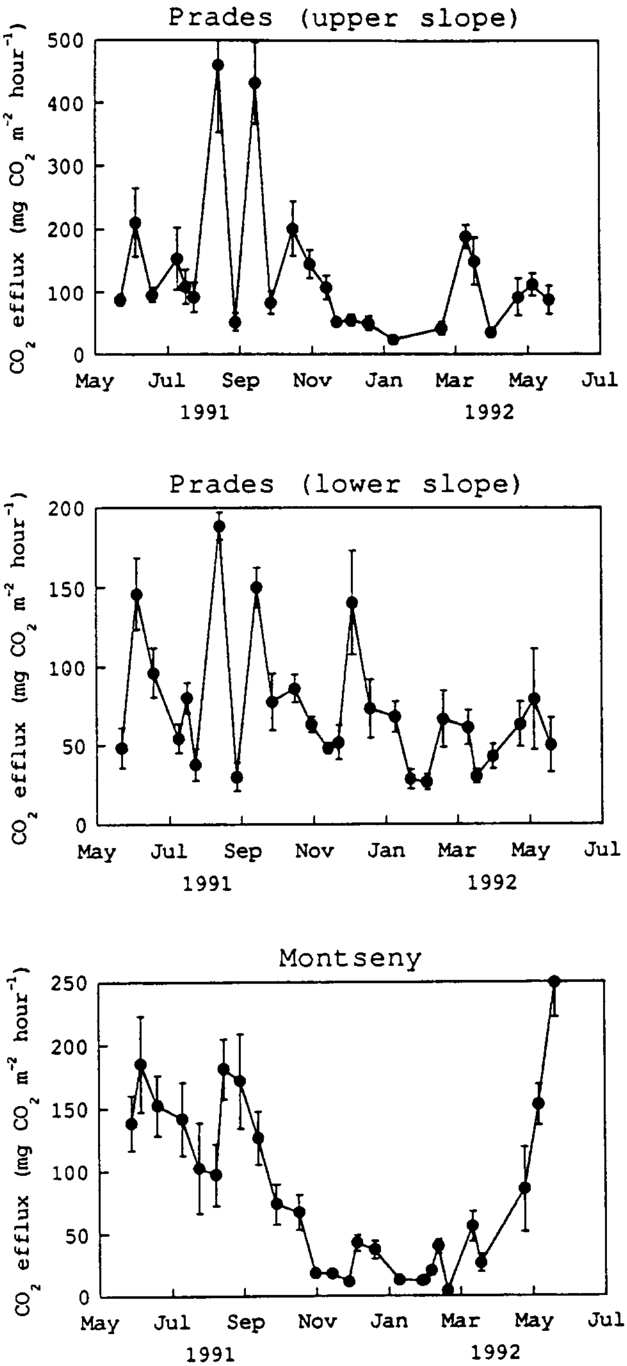

Fig. 3. Time course of soil CO_2 efflux at the three study sites. Each point is the mean of five replicate chambers. Vertical bars indicate the standard error.

Soil temperature and moisture

Soil temperatures were rather similar at the three sites: mean annual soil temperatures at 10 cm were 10.9 °C, 11.6 °C, and 11.1 °C at Montseny and Prades lower and upper slope, respectively.

Soil moisture was similar in the two Prades sites. Despite the higher rainfall at Montseny (precipitation was 665 mm at Prades and 908 mm at Montseny during the study year), gravimetric water content of the 2 mm sieved upper soil was lower at Montseny than at Prades (Fig. 2) in both summer and winter, probably because of the more sandy texture of the soil at Montseny. Annual mean soil moisture of the upper soil was 25%, 39% and 38% at Montseny and Prades lower and upper slopes, respectively.

Soil CO_2 efflux

Seasonal patterns of soil CO_2 efflux varied among sites (Fig. 3). At Montseny, soil CO_2 efflux showed a clear seasonal variation. Highest values were observed in late spring and late summer. During mid summer there was a decrease in CO_2 efflux. In winter, CO_2 efflux was very low. At Prades the seasonal pattern was not so clear (Fig. 3) but the main trends observed at Montseny were also present at both Prades sites. The two major differences between the seasonal variation of CO_2 efflux at Prades and Montseny were: (1) CO_2 efflux decreased much more noticeably at Prades during mid summer, but it increased suddenly to the highest measured values just after two summer storms, especially in the upper slope site; and (2) during the cold season, CO_2 efflux was higher at Prades than at Montseny. During the warm season (May to September) mean soil CO_2 efflux (mg CO_2 m^{-2} $hour^{-1}$; ±S.E. among monthly means) was 146 ± 15 at Montseny, 92 ± 14 at Prades lower slope, and 176 ± 34 at Prades upper slope. Corresponding values for the cold season (November to March) were: 26 ± 6, 59 ± 12, and 64 ± 18.

The annual mean soil CO_2 efflux was obtained at each site by first averaging the results for each calendar month and then averaging the monthly means. Annual mean soil CO_2 efflux (mg CO_2 m^{-2} $hour^{-1}$; ± S.E. among monthly means) was 83 ± 18 at Montseny, 75 ± 9 at Prades lower slope, and 122 ± 22 at Prades upper slope. Hence, annual mean soil CO_2 efflux varied more between two topographic positions within a single small catchment, than between comparable topographic positions in two different mountain ranges.

The previous estimates must be carefully evaluated. They are based on 24–27 fortnightly, short-term (ca. 2 hours per site each sampling date) measurements of CO_2 efflux made at the same time of the day. Nevertheless, averaging across all sites, the mean CO_2 efflux derived from six measurements in each

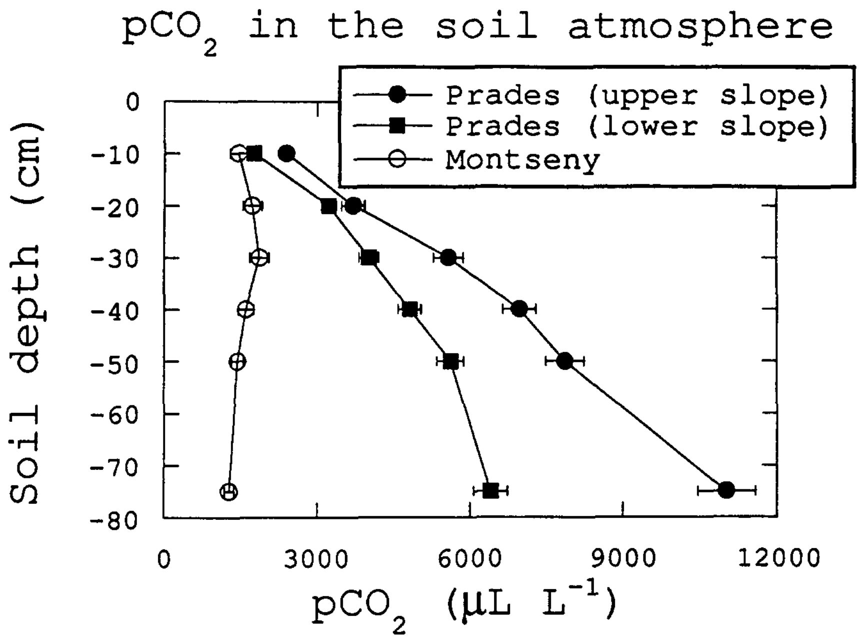

Fig. 4. Mean annual vertical profile of soil pCO_2 at the three study sites. Horizontal bars indicate the standard error among the different sampling dates.

of 10 diel studies (six measurements per diel cycle at each site) was 87 ± 17 mg CO_2 m^{-2} $hour^{-1}$ (unpub. data), which compared favourably with our midday estimate (74 ± 11 mg CO_2 m^{-2} $hour^{-1}$).

pCO_2 in the soil atmosphere

The mean value of soil pCO_2 in the vertical profile showed a maximum at 30 cm in the Montseny site (Fig. 4). At both Prades sites, pCO_2 increased with depth: the maxima were observed at the maximum measured depth (75 cm). Mean pCO_2 was higher at Prades than at Montseny for all soil depths. At 75 cm depth the mean pCO_2 at Montseny was only 12% of that measured at Prades upper slope, and 20% of that of Prades lower slope.

Annual variation of pCO_2 in the soil profile (Fig. 5) was similar to the annual variation of CO_2 efflux. Highest values of soil pCO_2 were measured in late spring-early summer and in late summer. Lowest values were measured in winter time. In general, there was a greater persistence of the pCO_2 vertical gradient at Prades than at Montseny. At Prades, pCO_2 minima and maxima were always observed at 10 cm and 75 cm respectively. At Montseny the vertical profile of pCO_2 was much more dynamic: about half the sampling dates gave pronounced maxima at 20–30 cm (Fig. 5). The other half, usually

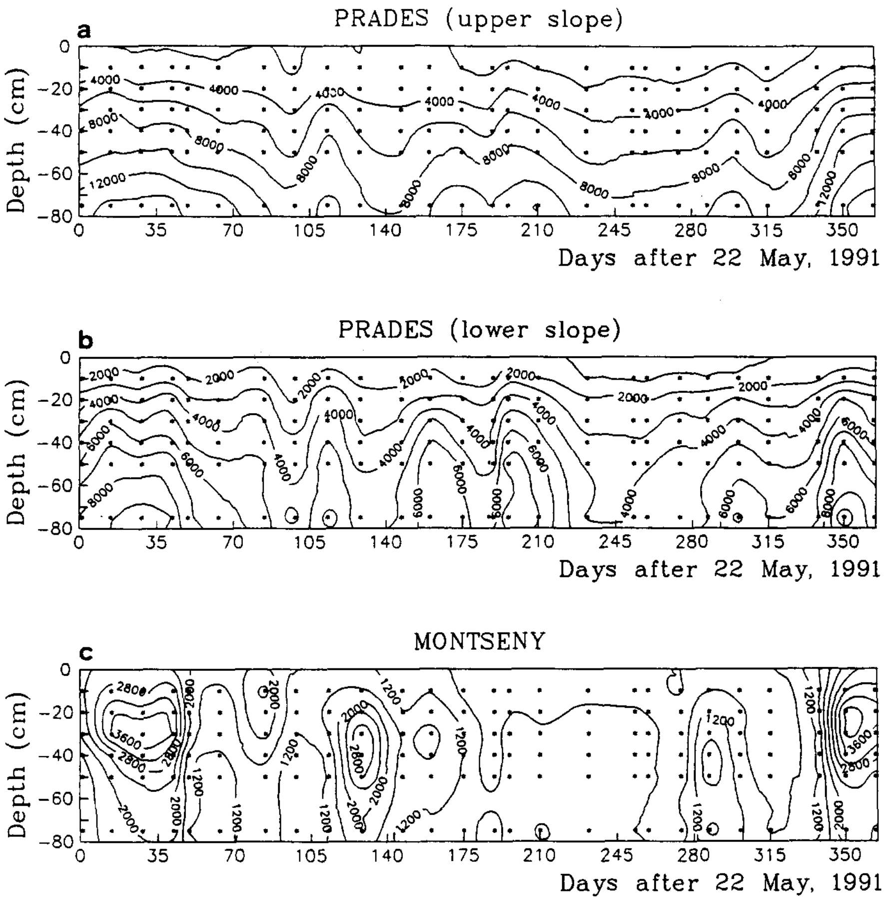

Fig. 5. Isopleths of pCO_2 in the soil atmosphere ($\mu L\ L^{-1}$) as a function of soil depth and time. (a) Prades upper slope; (b) Prades lower slope; (c) Montseny. Each measurement (marked with an asterisk in the diagrams) was the mean of three replicate access tubes. Isopleths were fitted by kriging.

occuring at lower soil pCO_2, showed either a practically uniform vertical profile of pCO_2 or increasing pCO_2 with depth. The lines of equal pCO_2 tended to be parallel to the vertical axis at Montseny, and to the time axis at Prades.

Relationship between soil pCO_2 and CO_2 efflux

Linear correlations between CO_2 efflux and soil pCO_2 at 10 cm (the depth at which these correlations were highest) were positive and significant (P <

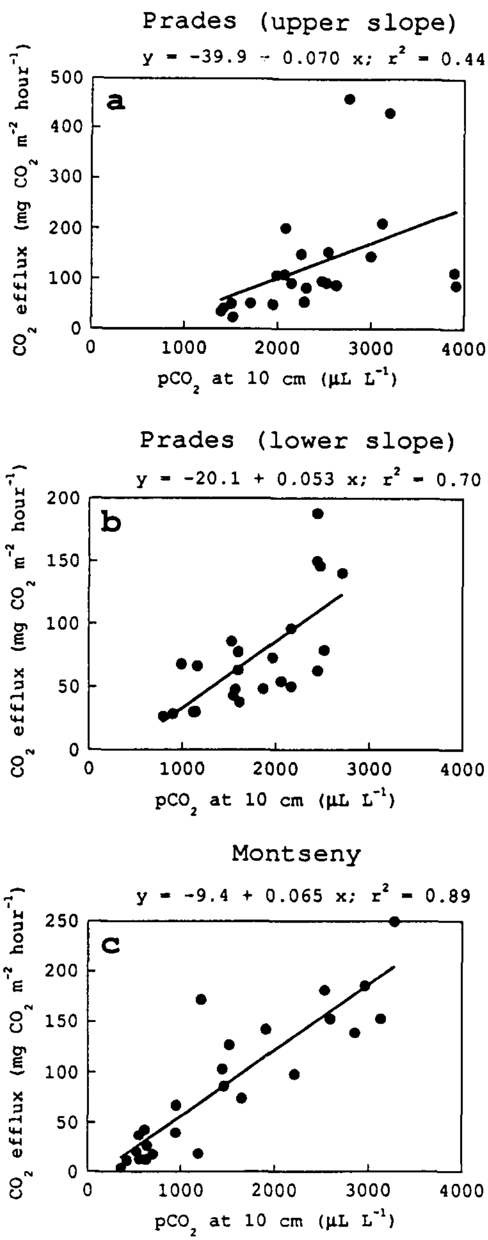

Fig. 6. Soil CO_2 efflux plotted against soil pCO_2 at 10 cm depth. (a) Prades upper slope; (b) Prades lower slope; (c) Montseny. Each dot is the mean of measurements at five chambers and three access tubes at a given sampling date. Least-squares linear regressions are shown.

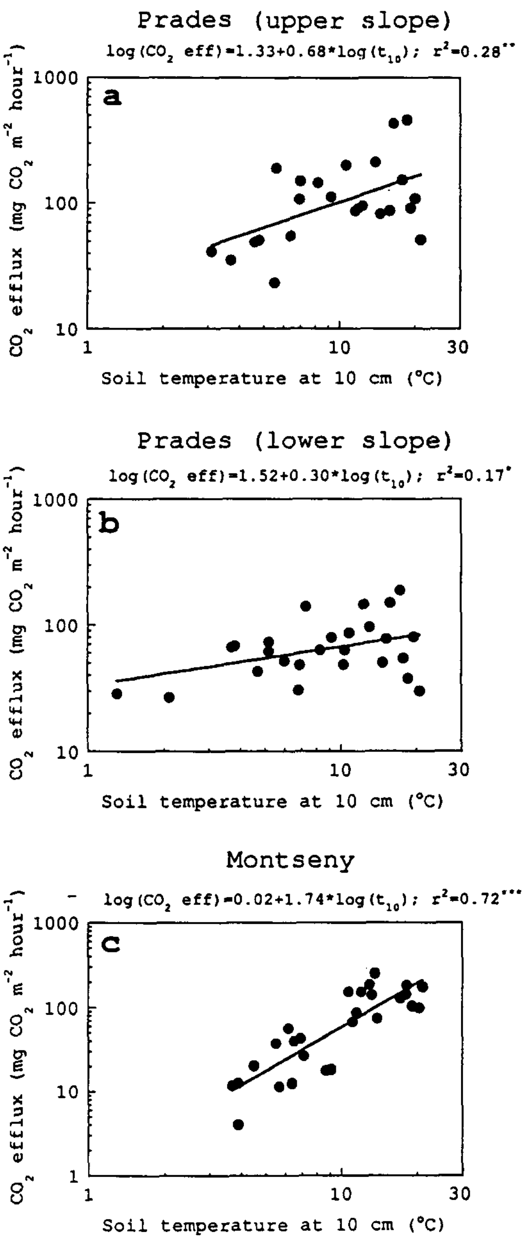

Fig. 7. Log-log plot of soil CO_2 efflux against soil temperature at 10- cm depth at the time of sampling. (a) Prades upper slope; (b) Prades lower slope; (c) Montseny. Least-squares power regressions are shown (* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$).

Table 3. Best-fitting equations obtained by stepwise multiple regressions of log (soil CO_2 efflux; mg CO_2 m^{-2} $hour_{-1}$) on log T10 (soil temperature at 10 cm, °C), gravimetric soil water content of the upper mineral soil (SW, %), and the product T10xSW. In parentheses, standard error of the regression coefficients.

Montseny		
log (soil CO_2 efflux)	=	$-2.412 + 3.536\ (0.67) \log T10 +$
		$+ 0.052\ (0.016)\ SW$
		$-0.003\ (0.001)\ T10 \times SW$
		$n = 23, r^2 = 0.816, S_{y.x} = 0.211, P < 0.0001$
Prades lower slope		
log (soil CO_2 efflux)	=	$1.467 + 0.0010\ (0.0003)\ T10 \times SW$
		$n = 22, r^2 = 0.34, S_{y.x} = 0.180, P = 0.004$
Prades upper slope		
log (soil CO_2 efflux)	=	$1.331 + 0.676\ (0.229) \log T10$
		$n = 24, r^2 = 0.28, S_{y.x} = 0.274, P = 0.007$

0.05) at all three sites (Fig. 6); the correlation was strongest at Montseny and weakest at Prades upper slope.

Relationships between soil CO_2 efflux and soil temperature and moisture

Soil CO_2 efflux was positively correlated with soil temperature at 10 cm (T10) at all three sites. The highest correlation coefficients were obtained using log-log regressions (Fig. 7). The relationship between log (CO_2 efflux) and log T10 was strongest at Montseny and weakest at Prades lower slope, and the slope of the regression was also higher at Montseny than at the Prades sites (Fig. 7).

Stepwise multiple regressions indicated that soil temperature, soil moisture, and their interaction significantly affected soil CO_2 efflux at Montseny (r^2 = 0.82, Table 3). At both Prades sites, the best fitting regression had a single independent variable and explained *circa* 30% of the variability: the soil temperature-moisture interaction for the lower slope, and temperature (log T10) for the upper slope.

Discussion

Seasonal variation of soil CO_2 efflux and pCO_2

Temperature is the main abiotic factor that controls soil CO_2 efflux in terrestrial ecosystems, although soil moisture is also important (Raich & Schlesinger 1992). The dependence of CO_2 efflux on temperature was stronger at Montseny than at Prades. At comparable topographic positions, soil CO_2 efflux was higher in summer and lower in winter at Montseny than at Prades, despite similar soil temperatures. Soil moisture was also important, particularly during the warm season, as evidenced by the significant interaction between soil moisture and temperature. Overall, soil CO_2 efflux at Montseny was more predictable (in terms of r^2) from soil temperature and moisture than at Prades, where CO_2 efflux varied more irregularly. In a Mediterranean-type shrub ecosystem in Greece (phrygana), the seasonal variation of CO_2 efflux was very similar to that found at Prades (Fouseki & Margaris 1981).

Soil pCO_2 showed a similar seasonal variation to that of CO_2 efflux. Hence, it was also affected primarily by soil temperature, and, to a lesser degree, by soil moisture. Other researchers obtained similar findings (Buyanovsky & Wagner 1983; Castelle & Galloway 1990; de Jong & Schappert 1972; Fernandez & Kosian 1987; Reardon et al. 1979; Rightmire 1974; Solomon & Cerling 1987). At our sites, particularly at Montseny, soil CO_2 efflux could be predicted reasonably well from pCO_2 at 10 cm.

Soil CO_2 efflux in comparison with other C fluxes within the ecosystem

Mean annual soil CO_2 efflux (g C m^{-2} $year^{-1}$) was 291 at Prades upper slope, 178 at Prades lower slope, and 197 at Montseny. These annual mean CO_2 effluxes can be compared to C fluxes in litterfall measured at Prades upper slope and at Montseny. (No litterfall data are available at Prades lower slope). At Prades upper slope, mean annual litterfall in a plot near our sampling site was 228 g dry weight m^{-2} $year^{-1}$ during a 7-year period (Bellot et al. 1992). Assuming C to be 50% of litter dry weight, this amounts to 114 g C m^{-2} $year^{-1}$. Our estimate of annual CO_2-C efflux at Prades upper slope is 2.7 times higher than this C flux in litterfall. For a wide range of ecosystems, ratios of annual C flux in soil CO_2 evolution to that in litterfall average 2.5 according to Schlesinger (1977) and 2.5–2.9 according to Raich & Schlesinger (1992). At Montseny, litterfall in a plot containing our sampling site averaged 200 g C m^{-2} $year^{-1}$ (Verdú 1984; Mayor 1990), compared to with our CO_2 efflux estimate of 197 g C m^{-2} $year^{-1}$. We think that our value of CO_2-C efflux at Montseny is too low, perhaps due to soil spatial variability.

Soil pCO_2

Maximum measured soil pCO_2 reported in the literature ranges from 0.6% (Castelle & Galloway 1990) to 7.0% (Buyanovsky & Wagner 1983). Maximum soil pCO_2 measured at Prades lies within this range (1.7% at the upper slope site; 1.1% at the lower slope), but that at Montseny is much lower (0.4%). Mean soil pCO_2 is also much lower at Montseny than at Prades for soil depths greater than 40 cm. These results suggest that the soil at Montseny is much better ventilated than at Prades.

Not only are the pCO_2 values different at the two study locations but the profile of soil pCO_2 with increasing soil depth is also markedly distinct. Atkinson (1977), Nakayama & Kimball (1988), Parada et al. (1983), and Solomon & Cerling (1987) found the maximum pCO_2 at the deepest measured point, as in the Prades sites. Contrarily, Buyanovsky & Wagner (1983), Castelle & Galloway (1990), de Jong & Schappert (1972), and Reardon et al. (1979) found the maximum pCO_2 at an intermediate depth, as we found at Montseny.

The large differences found in soil pCO_2 for this study and in the shape of pCO_2 vertical profiles at Prades and Montseny were totally unexpected given the broad similarity of soil type, vegetation and CO_2 efflux. Many authors assume that the main mechanism of soil aeration is molecular diffusion of CO_2 from the soil to the atmosphere (Cerling 1984; de Jong & Schappert 1972; Hendry et al. 1993; Hesterberg & Siegenthaler 1991; Solomon & Cerling 1987). Following these authors, we attempted to model the vertical profiles of pCO_2 observed at Prades and Montseny using the standard theory of gas diffusion, and the values of CO_2 production (CO_2 efflux), soil moisture, and soil porosity measured at the three different sites.

Model structure

The soil column was assumed to have a depth of 80 cm and it was discretized in 8 soil layers of 10 cm each. The transport of CO_2 by diffusion between two contiguous layers is given by (Hillel, 1980):

$$\partial c/\partial t = \partial/\partial z[D_s(\partial c/\partial z)] + P \qquad (1)$$

where c is the concentration of CO_2, t the time, D_s the diffusion coefficient of CO_2 in the soil, z the vertical space variable, and P the production rate of CO_2. D_s was calculated as a function of the air-filled soil porosity (f_a) using the formulation proposed by Marshall (1959), cited by Hillel (1980):

$$D_s = D_0 * f_a^{1.5}$$

where D_0 is the diffusion coefficient of CO_2 in air and f_a is calculated as:

$$f_a = f - \theta$$

Table 4. Data used to run the simulation model of CO_2 diffusion.

	Montseny	Prades lower slope	Prades upper slope
f ($cm^3\ cm^{-3}$)	0.46	0.50	0.50[a]
θ ($cm^3\ cm^{-3}$)	0.11	0.20	0.18
f_a ($cm^3\ cm^{-3}$)	0.35	0.30	0.32
T (°C)	10.9	11.6	11.1
D_0($cm_2\ s^{-1}$)	0.15	0.15	0.15
D_s($cm^2\ s^{-1}$)	0.031	0.025	0.027
P(mg CO_2 $m^{-2}hour^{-1}$)	83	75	122

[a] The same value as for Prades lower slope was used, because there were not significant differences between both sites in total porosity at the same soil depth, and the model considers a soil depth of 80 cm (i.e. similar to that of Prades lower slope). Mean values given in Table 2 are affected by differences in total soil depth.

where f is the total porosity and θ is the volume wetness, that in turn is calculated from the measured gravimetric water content of the 2 mm-sieved soil (w) taking into account the soil bulk density (D_b) and stoniness (st):

$$\theta = w * (1 - \mathrm{st}) * D_b$$

D_0 is calculated from (de Jong & Schappert, 1972):

$$D_0 = 0.139 * (T/273)^2$$

where T is the soil temperature (°K).

Production of CO_2 in the soil profile was assumed to decrease with depth following a negative exponential function (Simunek & Suarez, 1993):

$$P_z = e^{-\alpha z}$$

where P_z is the CO_2 production at depth z, and α is an empirical constant. As the exponential function is infinite and the depth of the soil is not, the distribution function P_z must be normalized, in order to insure that the total CO_2 production (P) was equal to the sum of the CO_2 productions of each individual soil layer (P_z).

Model application

The vertical distribution of CO_2 production was unknown at all sites, so it was adjusted for each site in order to get the best fit between the simulated and the mean measured pCO_2. Total porosity, temperature, moisture, and consequently the diffusion coefficient, were considered to be constant through depth. The model was run for the Montseny, Prades upper slope, and Prades

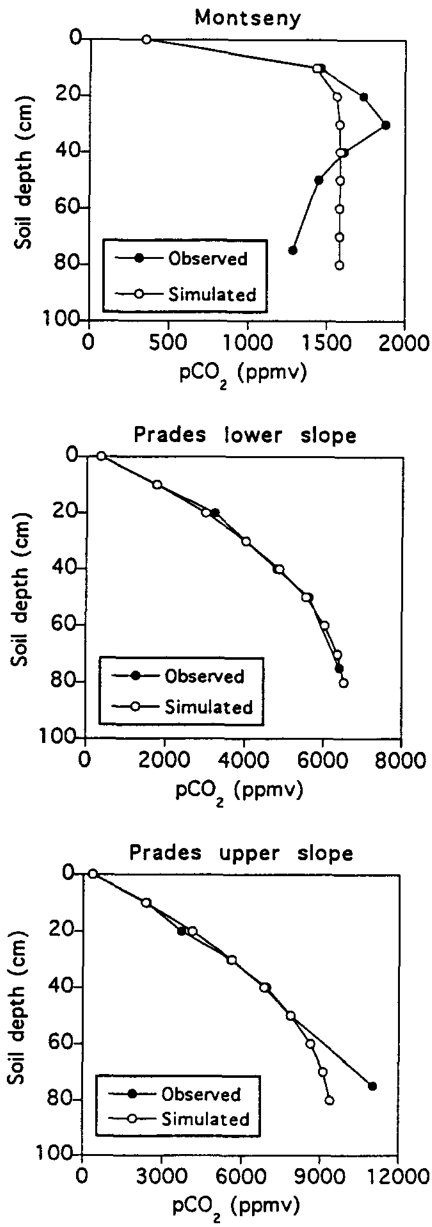

Fig. 8. Simulated vertical profile of pCO_2 compared to observed mean values. Model parameters are those of Table 4.

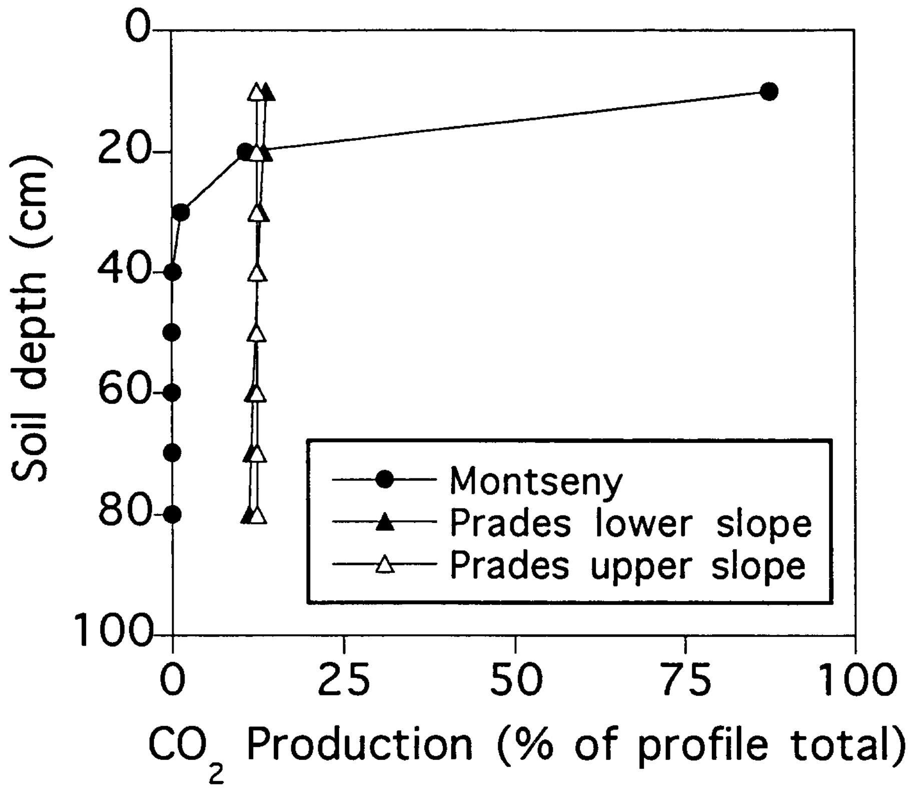

Fig. 9. Optimized vertical profiles of CO_2 production in the soils of Montseny and Prades used to produce the results showed in Fig. 8.

lower slope sites considering as many actually measured variables as possible (Table 4).

Initial and boundary conditions for the solution of equation 1 were: (1) An initial constant vertical distribution of pCO_2 equal to 350 ppmv. (2) An upper boundary condition that considers that the uppermost soil layer diffuses to an atmosphere of a constant pCO_2 of 350 ppmv. (3) A lower boundary condition that considers an impermeable layer (D_s = 0) below the 80 cm soil layer.

Equation 1 was solved using a fully explicit scheme. The time increment (Δt = 900 s) was chosen in order to satisfy the heuristic stability criterion given by Press et al. (1986, p. 639):

$$\Delta t < \Delta x^2/2D_s$$

The model was run for a period of 30 days considering all the variables constant through this time. In practice this means that the equilibrium vertical distribution of pCO_2 is obtained, as for the considered D_s, pCO_2 become stable before 10 days.

Model results

The model reproduced quite well the observed mean vertical profile of pCO_2 in the soil atmosphere of both Prades soils, but not that of Montseny (Fig. 8). The optimized values of the parameter that describes the exponential decay of CO_2 production with depth (α) were very different for the Montseny and Prades soils (Fig. 9). CO_2 production at the Montseny site seemed to be concentrated in the uppermost 20 cm of the soil, whereas at Prades, CO_2 production appeared to be homogenuous throughout the soil profile.

At the Montseny site, living plus dead roots of less than 2 mm in diameter had a biomass of 2.0 t d.w. ha^{-1} at 0–20 cm, 1.3 t ha^{-1} at 20–40 cm, and 0.7 t ha^{-1} at 40–60 cm (Canadell & Rodà, 1991). According to these results root activity appears to be concentrated in the upper soil at Montseny, and the optimized vertical distribution of CO_2 production at Montseny seems to be quite reasonable. Unfortunately, no similar data are available for the Prades sites. Nevertheless, it can be hypothesized that being Prades a more xeric area than Montseny, root activity can be displaced to higher depths in order to extract water from deeper soil layers.

The model structure allowed for three major sources of between-site differences in the vertical distribution of pCO_2, namely of: (1) differences in parameters that affect CO_2 diffusivity (total porosity and volume wetness), (2) differences in the vertical distribution of CO_2 production, and (3) differences in CO_2 total production. In order to see which one of these factors was the most important to explain the observed differences between sites, the model was further run for a given site using at each run the value of one of the above-mentioned factors corresponding to another site, and the other two of the considered site:

Prades lower slope *vs.* Montseny (Fig. 10 top). As the total CO_2 efflux at these two sites was very similar (Table 4), the simulation at Prades lower slope with the Montseny total CO_2 production did not change very much the simulated pCO_2 (line C). Contrarily, both D_s and, especially, the vertical distribution of CO_2 production greatly affected the vertical profile of pCO_2 (lines A and B, respectively).

Prades lower slope *vs.* Prades upper slope (Fig. 10 bottom). The higher total CO_2 production at the upper slope site appeared to be the reason for the higher pCO_2 observed at the Prades upper slope site (line F). D_s and the vertical distribution of CO_2 production (lines D and E) were not different enough between these two sites to change appreciably the simulated vertical profile of pCO_2.

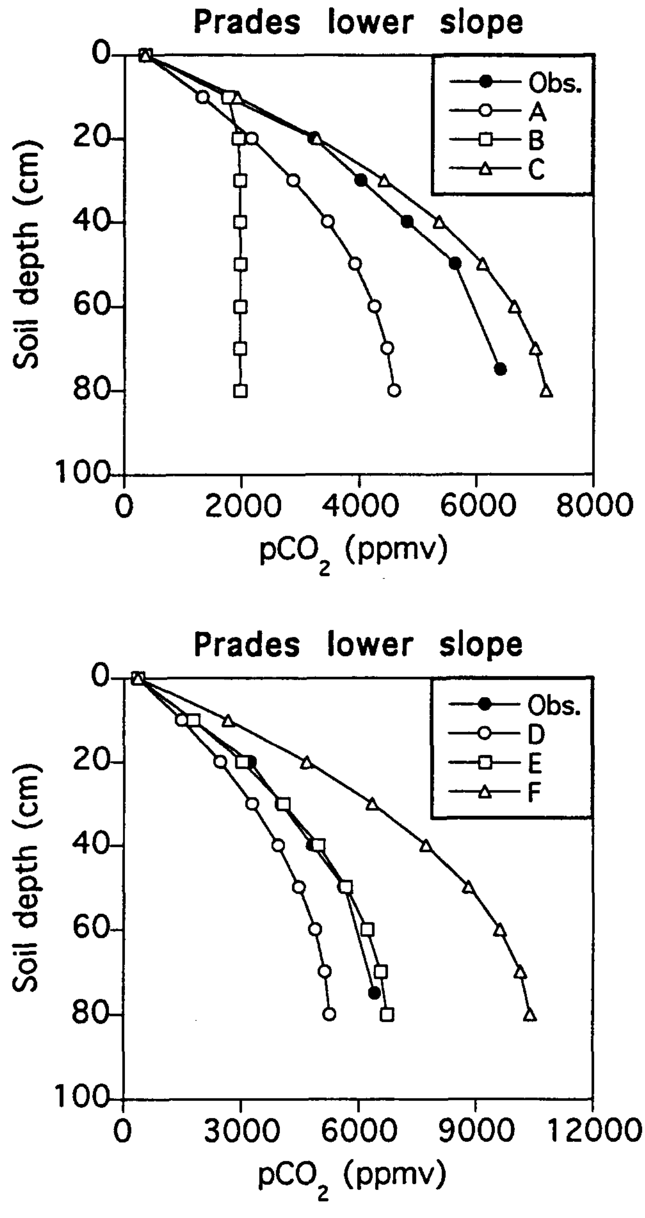

Fig. 10. Effect of changing parameters in the simulated vertical profile of pCO_2 compared to the mean observed values at the Prades lower slope site. In the upper diagram one parameter corresponding to the Montseny site was used, and in the lower diagram one parameter corresponding to the Prades upper slope site was used. All other model parameters were those of Prades lower slope site. A: D_s of Montseny. B: α of Montseny. C: P of Montseny. D: D_s of Prades upper slope. E: α of Prades upper slope. F: P of Prades upper slope.

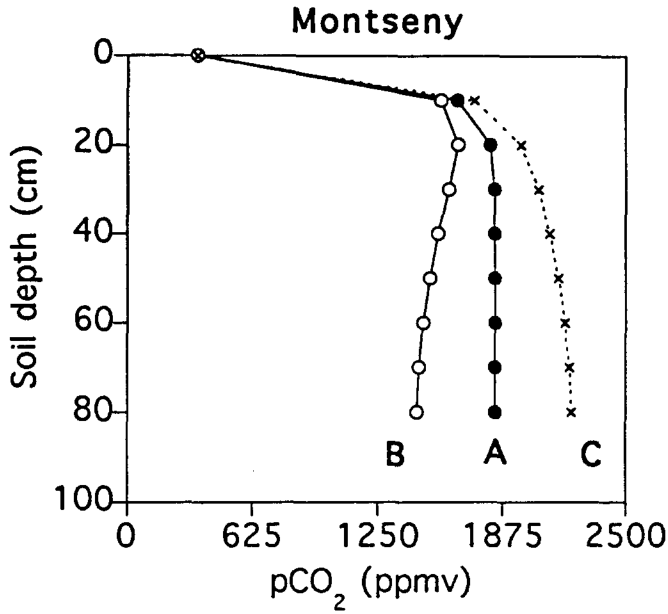

Fig. 11. Simulated vertical profile of pCO_2 obtained using a time variable CO_2 production rate; all the other model parameters are those corresponding to the Montseny site shown in Table 4. (A) Constant CO_2 production: 30 days at 100 mg CO_2 m^{-2} $hour^{-1}$. (B) Increasing CO_2 production: 25 days at 0 CO_2 m^{-2} $hour^{-1}$ followed by 5 days increasing linearly from 0 to 100 mg CO_2 m^{-2} $hour^{-1}$. (C) Decreasing CO_2 production: 25 days at 200 CO_2 m^{-2} $hour^{-1}$ followed by 5 days decreasing linearly from 200 to 100 mg CO_2 m^{-2} $hour^{-1}$.

According to the model results, gas diffusion theory was able to explain why soil pCO_2 was much higher at Prades than at Montseny, and to reproduce the shape of the vertical profile of pCO_2 at the Prades soils. Nevertheless, the model failed to simulate the soil pCO_2 maximum found at 20–30 cm depth at the Montseny site. In fact, there is not any parameter combination that could produce such a maximum at equilibrium, unless the model was modified considering an unrealistic CO_2 sink at depth (a realistic sink of CO_2 could be justified by the amount of CO_2 that dissolves into groundwater – around 1% of the total CO_2 flux –, but it only produces a slight decrease of the simulated pCO_2 at 75 cm depth). So, non-equilibrium situations must be considered to explain such kind of vertical profile of soil pCO_2. Suarez and Simunek (1993) obtained vertical profiles of pCO_2 with a pronounced intermediate maximum after 100 days, but their model required a low CO_2 diffusivitiy, and consequently, the calculated pCO_2 was very high (5–15%). Obviously, this is not the case at Montseny, where diffusivity is high and the measured pCO_2 was much lower.

A more realistic possibility would be to consider a temporally variable CO_2 production rate. The simulated vertical profile of pCO_2 was very different if the CO_2 production rate was either constant, increasing, or decreasing over time. Using the Montseny parameters, the model calculated a vertical profile of pCO_2 with an intermediate maximum when CO_2 production rate was increasing over time (Fig. 11, line B), whereas the pCO_2 profile did not show such a maximum when CO_2 production rate was decreasing over time (Fig. 11, line C) or it was constant (Fig. 11, line A). Unfortunately, our field measurements were not detailed enough to investigate the short-term variation in CO_2 production rate and in the vertical pCO_2 profile. This simple exercise showed that transient situations can give quite different results than the simpler consideration of equilibrium situations. Taking into account that CO_2 production rate in soils is always changing, both seasonally and daily, pCO_2 in the soil atmosphere might be never at equilibrium. The relative difference between transient and equilibrium situation would be more noticeable in soils with a low pCO_2, like Montseny, than in soils with a high pCO_2, like Prades.

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