



## C and N stable isotope inventories in CO<sub>2</sub>, CH<sub>4</sub>, DOC, DON, and peat solid phase in three southern Patagonian ombrotrophic bogs

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Peatlands in Southern Patagonia have become the focus of a small, yet increasing number of studies. Large, pristine bogs and mires provide archives of the past climate and environmental conditions. Therefore, researchers have investigated peat accumulation, decomposition, and vegetation changes to elucidate the history of this landscape.

In peatlands, analysis of stable isotopes of carbon and nitrogen has been increasingly used to study peat accumulation, decomposition, past environmental conditions, and biogeochemical processes. Yet available studies so far were almost exclusively carried out in northern peatlands and there is limited knowledge about carbon and nitrogen isotope patterns in southern peatlands. To interpret shifts in isotopic composition of solids and solutes, typical profiles and levels of variation at various locations need to be known. Therefore we investigated three ombrotrophic bogs in Southern Patagonia for isotopic composition of dissolved CO<sub>2</sub> and CH<sub>4</sub>, DOC, DON, and peat solid phase C and N. The three sites differed in terms of precipitation, vegetation, and exposition to sea-spray input.

Values of  $\delta^{13}\text{C}$  in the peat of the driest site were between -27 to -26 per mil with a slightly increasing trend with depth down to 150 cm, and decreased to -28 per mil below (sampling depth 300 cm). DOC had almost similar isotopic composition as the solid phase (diff. < 0.5 per mil) in the upper 150 cm and was about 1 per mil enriched in  $^{13}\text{C}$  below that depth. At the site with intermediate precipitation, we found a  $\delta^{13}\text{C}$  in the solid phase of about -26 per mil in the upper profile, slightly decreasing with depth to about -27 per mil in 300 cm. Here, DOC was depleted in  $^{13}\text{C}$  (0.5 to 1 per mil) in the upper part, but adjusted to the signatures of the solid phase in 200 cm depth. This pattern was also observed at the wettest site. Nevertheless, we could neither identify clear common trends, nor attribute certain factors to the shifts in isotopic composition. All variations were within reported ranges for typical peatland vegetation even under similar environmental conditions. Values of  $\delta^{15}\text{N}$  in the peat solid phase were around 0 per mil at all sites, regardless of depth. Contrarily, in the DON there was an obvious enrichment of  $^{15}\text{N}$ , ranging from 1 to >15 per mil, that increased with depth. We attribute this enrichment of  $^{15}\text{N}$  in DON to multiple recirculations and a high proportion of microbial N in this pool, while the light isotopes are preferentially mineralized.

Isotopic composition of dissolved gases ranged from -23 to +4 per mil for CO<sub>2</sub>, increasing with depth, and from -75 to -63 per mil for CH<sub>4</sub>, more or less following the CO<sub>2</sub> signature. The  $\delta^{13}\text{C}$  of CO<sub>2</sub> was thus dominated by methanogenic activity, leading to residual  $^{13}\text{C}$  enrichment. This was further supported by fractionation factors  $a\text{C}$  between CO<sub>2</sub> and CH<sub>4</sub> in a range of 1.050 to 1.075, suggesting dominance of hydrogenotrophic methanogenesis. Interestingly, at all sites fractionation factors converged to about 1.070 at a depth of 100 cm, which is probably linked to a thermodynamic limitation of the methanogens, according to available microbiological studies.

In summary, this study showed relatively small variations in carbon isotopic signatures of solids and DOC, despite obvious differences of the sites in terms of climate, decomposition, and vegetation. Interpretation of such data in light of paleoclimatic conditions thus needs to be done with care. While  $\delta^{15}\text{N}$  in the solid phase was relatively constant, the shifts in DON may merit more attention. Isotopic composition of dissolved gases was comparable to previous studies and typical for methanogenic environments.