



## Nonexchangeable H isotope ratios of soil organic matter across different ecoregions in Argentina

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$\delta^2\text{H}_{n(\text{nonexchangeable})}$  analyses of bulk soil organic matter (SOM) are analytically challenging because they require separation of organic matter (OM) and mineral matrix and isotopic equilibration of exchangeable H (Sauer et al. 2009, Ruppenthal et al. 2010). However, isolation of SOM for  $\delta^2\text{H}_n$  analysis is necessary in order to avoid ambiguities in the interpretation of soil  $\delta^2\text{H}_n$ , which constitutes a mixed signal of  $\delta^2\text{H}_n$  of SOM and  $\delta^2\text{H}_n$  of pedogenic clay minerals. For the first time, we were able to determine  $\delta^2\text{H}_n$  values of pure SOM, isolated from 53 topsoil samples from 18 sampling sites along a 2500-km north to south transect from the Argentinean Pampas to the Patagonian Steppe. We demineralized soil samples with a new hydrofluoric acid (HF) demineralization technique optimized for high OM recovery and water-steam equilibrated the SOM concentrates prior to  $\delta^2\text{H}$  measurement.

Spiking of demineralization reagents with deuterated water had no effect on  $\delta^2\text{H}_n$  values (-96 to -119‰ for demineralization with deuterated reagents vs. -92 to -117‰ for conventional demineralization), proving the suitability of HF treatment for preparation of SOM concentrates for  $\delta^2\text{H}_n$  analyses. Standard deviation of independently demineralized and equilibrated replicate samples was below 4‰ indicating very good reproducibility of both HF demineralization and H isotope equilibration.

$\delta^2\text{H}_n$  of SOM varied between -71 and -161 ‰ and showed a close relationship to modelled annual average  $\delta^2\text{H}$  of local precipitation at the sampling sites ( $\delta^2\text{H}_{n\text{SOM}} = 1.18 \delta^2\text{H}_{\text{precipitation}} - 41$ ,  $r=0.97$ ,  $p<0.0001$ ). This result was unexpected because of the large variation of vegetation, soil type and climatic conditions along the sampling transect. The very robust relationship suggests that  $\delta^2\text{H}_n$  of bulk SOM can be predicted solely from modelled  $\delta^2\text{H}$  of local precipitation and that effects such as enrichment of  $^2\text{H}$  in soil and leaf water in arid regions, physiological effects in plants or possible isotope fractionation during SOM decomposition do only marginally affect  $\delta^2\text{H}_n$  of bulk SOM. Analysis of  $\delta^2\text{H}_n$  of SOM could therefore help to reliably constrain the geographical origin of soil samples and, with an extended database, offer the perspective to model a SOM  $\delta^2\text{H}_n$  isoscape from the Global Network of Isotopes in Precipitation (GNIP)  $\delta^2\text{H}$  data.

### References

- Ruppenthal et al. 2010 *Geoderma* 155, 231-241
- Sauer et al. 2009 *Rapid Commun. Mass Spectrom.* 23, 949-956