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Halogens (Cl and Br) accumulation in podzols from NW Spain

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Halogens and halogenated organic compounds have been found to play a relevant role in the environment, from atmospheric chemistry (destruction of O_3, Hg cycle) to human health (carcinogenic effects, damages to the endocrine system). This has led to an increasing interest in the study of their fate in natural environments. Until very recently halogens were thought to be non reactive in soils, but in the last two decades it has been demonstrated that the formation of organohalogens is ubiquitous in nature. The retention of halogens by soils is coupled to the transformations of the organic matter by microbial enzymatic processes mediated by haloperoxidases. Thus soils may be important sinks of halogens and other halogenated compounds. Podzols in patricular have the potential of sequestering halogens if their inventories were to be dominated by organohalogenated species.

To test this hypothesis we have analyzed two podzols from NW Spain. The soils were sampled each 5 cm, to provide a high vertical resolution. Total Cl and Br were determined by XRF in air-dried and ashed samples (after 12 hours at 550ºC); C and N were analyzed with a LECO TruSpec CHN analyser. Fractionation of Al, Fe, Mn, and Si was evaluated using selective dissolution techniques: KCl, $LaCl_3$ and $CuCl_2$ extracts for Al (Al_K, Al_{La}, Al_{Cu}); Na-pyrophosphate, acid NH4-oxalate and NaOH for Al, Fe, Mn and Si (Al_{PY}, Mn_{PY}, Fe_{PY}, Al_{OX}, Mn_{OX}, Fe_{OX}, Al_N, Si_N); and concentrations in the extracts were measured by AAS.

Average Cl concentrations were highest in the A horizon (650 $\pm$249 μg g^{-1}) and a

secondary maximum was found in the spodic horizon (255 ±177 μg g^{-1}); the lowest concentration was found in the BwC horizon (107±89 μg g^{-1}). For Br the highest concentration occurred in the spodic horizon (152 ±46 μg g^{-1}) and the lowest in the E horizon (5.5±3.5 μg g^{-1}). No chlorine was detected in the ashed sampled and only low concentrations of Br (usually not exceeding 10 μg g^{-1}) corresponding to less than 10% the original concentration.

Chlorine showed significant positive correlations to C (r 0.87) and the proportion of Al-humus complexes of moderate stability ([Al$_{Cu}$-Al$_{La}$]/Al$_{PY}$)(r 0.72), and a negative correlation to the proportion of high stability Al-humus complexes ([Al$_{PY}$-Al$_{Cua}$]/Al$_{PY}$)(r -0.75). Br showed a significant correlation to C content but in two different groups: one comprising the A and E horizons (r 0.95) and another including the samples of the B horizons (r 0.99). Bromine was also highly correlated to Al-humus complexes, in particular to those of higher stability (r 0.96). These results suggest that the inventory of both elements in the studied podzols must be dominated by organo-chlorinated and organo-brominated compounds and that they are subjected to downward migration and enrichment during podzolisation. The degree of halogenation of the organic matter (estimated by the halogen/carbon molar ratios) indicate differences for both elements coherent with their possible affinity for different organic matter pools: average chlorination increases from the A to the E horizon (A 7.0 ±2.6, E 13.7 ±8.9 mmol Cl/mol C) and then decrease with depth (EB 12.2 ±10.9, Bhs 6.3 ±1.3,Bs 8.2 ±1.3 and Bw-BwC 7.7±5.7 mmol Cl/mol C); while the degree of bromination increases from the A to the spodic horizon and remains high in the deeper soil (A 0.10 ±0.01, E 0.16 ±0.04, EB 0.32 ±0.06, Bhs 1.07 ±0.41, Bs 1.49 ±0.10, Bw-BwC 1.22± 0.15 mmol Br/mol C). In consequence Br is relatively enriched compared to Cl, and the Cl/Br ratios decrease by an order of magnitude from the surface soil (30-40) to the bottom soil horizons (3).

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