The use of mosses as bioindicators for Zn pollution: Physico-chemical characterization and stable isotopic fractionation

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Bioindicators have been used in urban and industrial areas to control the atmospheric pollution. In this sense, mosses are most efficient because they have the capacity to reflect the chemical composition of the environment where they inhabit. This research work is focused in the role of four native mosses (*Hypnum sp*., *Sphagnum sp*., *P. purum* and *B. rutabulum)* as bioindicator for Zn pollution in Europe, via& combining physico-chemical characterization of moss surfaces and measuring Zn isotopic fractionation between mosses and aqueous solution.

The acid–base titrations were performed for a pH range from 3 to 10. The pH values of the zero net proton adsorption (pH_{PZC}) were equal to 5.01 ± 0.13 (*Hypnum sp*.), 4.64 ± 0.10 (*Sphagnum sp.),* 4.96 ± 0.14 (*P. purum*) and 6.23± 0.25 (*B. rutabulum*). *B. rutabulum* showed the highest excess of adsorbed protons (0.21mmol L^{-1}), whereas *Sphagnum sp*. exhibits the highest negative surface charge. Consequently *Sphagnum sp*. may be the most efficient cation adsorbent, as it has the highest number of negatively charged moieties on the surface. The results of surface complexation modeling of all four moss species suggested the presence of several functional groups: phosphodiester (pK a= 3.6–3.7), carboxyl (pK_a = 4.7–5.7), phosphoryl (pK_a =5.9–7.4), amine (pK_a = 7.7–9.2) and polyphenols (pK_a =10.1–10.4). The pH-edge adsorption studies yielded the maximal adsorption as 73% at pH = 7.8 for all the species, following and "universal adsortpion edge". The degree of Zn adsorption can be ranked as following: *B. rutabulum* ≥ *Sphagnum sp*. ≥ *Hypnum sp*. ≥ *P. purum*. The langmuirian studies demonstrated that the species could be ranked as: *B. rutabulum* ≥ *Sphagnum sp*. ≥ *P. purum* ≥ *Hypnum sp*. Where *Sphagnum sp*. showed the maximum number of binding sites (28.6 mmol g^{-1}). All the species presented a similar maximum adsorption capacity (q_{max}) that was from 0.7 to 1.1 mmol g^{-1}.

The isotopic fractionation of Zn during *Sphagnum* sp. adsorption experiments is within 0.3 ‰ for ^{66}Zn. Therefore, mosses can be used as strightforward tracers of environmental pollution since there is very little modification of the isotopic signature of Zn source during Zn uptake or adsorption on moss bags from the aerosols.