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Lithium and Boron isotopic compositions of rainwaters in France: origin and spatio-temporal characterization

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We report lithium (Li) and boron (B) concentrations and isotope measurements for 45 monthly rainwater samples collected from four different sites in France, from coastal and interior locations (Brest, Dax, Orléans and Clermont-Ferrand) corresponding to an annual sample collection. This study is the first investigation for both Li and B isotope ratios in rainwater samples collected over a long time period at a national scale. We have measured the range of Li and B isotopic variations in these rainwaters in order to determine the origin of these elements in rainwaters and to characterize both the seasonal and spatio-temporal effects for δ^7Li and δ^{11}B signatures in rainwaters. Lithium and boron concentrations are low in rainwater samples and are ranging from 0.004 to 0.292 μmol/L and from 0.029 to 6.184 μmol/L, respectively. In addition, δ^7Li and δ^{11}B values in rainwaters present also a great range of variation between +3.2 and +95.6‰ and between -3.3 and +40.6‰ over a period of one year, respectively for δ^7Li and δ^{11}B, clearly different from the signature of seawater. Our study also highlights that seasonal effect (i.e. month of precipitation or rainfall amount) is not the main controlling factor for both elemental concentrations and isotopic variations. δ^7Li and δ^{11}B values in rainwaters are clearly different from one site to another highlighting the variable contribution of sea salts in the rainwater according to the sampling site (coastal vs. inland: also called the distance-from-the-coast-effect). This feature is well illustrated when the wind direction is also investigated for each sample location (origin of air masses). The most striking outcome of this study is that seawater is not the main supplier for dissolved atmospheric lithium and boron, and non sea salt sources (i.e. crustal, anthropogenic and biogenic sources) should also be taken into account when Li and B isotopes are considered in hydrogeochemistry as an input to surface waters and groundwater bodies as a recharge.