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Biogeochemical Fluxes of Manganese in a Central - Bohemian Forested Catchment on Granite Bedrock

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Cycling of Mn in the environment is affected considerably by plant metabolism. Exogenous geochemistry of Mn, its content, and fluxes have been studied in Lesní potok, a small catchment (0.765 km^2) located approximately 30 km SE of Prague. The forested area (*Fagus*, *Carpinus* and *Picea* dominated) is underlain by granitoids of the Říčany Massif, coarse-grained biotitic monzogranite, and fine-grained two-mica syenogranite. The occurrence of Mn depends on the mafic component, and biotite (mean content 8.1-vol. %) is the main Mn-bearing phase.

Input of Mn is mediated by atmospheric deposition and weathering of the underlying rock. (Skřivan *et al.*, 1995). Bulk precipitation samples have been collected monthly since May 1989 to quantify the former flux. Dissolved- and weakly bound Mn were differentiated. Mean annual flux of Mn through the atmospheric deposition (D_{Mn}, mg m^{-2} yr^{-1}) was 11.9 with annual values ranging from 8.3 to 15.9 (1990-1996). The values of D_{Mn} do not correlate with the annual precipitation height.

Export from the catchment by means of surface discharge has been monitored since June 1993. The annual output of Mn (O_{Mn}, mg m^{-2} yr^{-1}) in 1994, 1995, and 1996 was 18.4, 36.3, and 43.0, respectively. Input/output budgets derived from measurements of the corresponding fluxes is negative, *i.e.*, more Mn is being exported than enters the catchment via atmospheric deposition. Depletion of the catchment Mn pool will occur unless it is balanced by weathering (in excess of approx. 20 mg m^{-2} yr^{-1}). The enhanced output of Mn from the catchment may be the result of increasing input of H^+ in acid precipitation, which gradually, may lead to the depletion of Mn in the catchment.

The metabolic role of Mn is manifested in the interaction of wet atmospheric precipitation with plant assimilation organs (*i.e.*, ion exchange of H^+ with the metabolic products), resulting in increased concentrations of Mn below the tree canopy - in the throughfall. To determine the flux of Mn in *Fagus/Carpinus* throughfall A net of samplers have been placed beneath a 50 year old mixed population since April 1994 (the deciduous trees cover 42 % of the catchment area). Complete data for 1995 and 1996 show that the flux of Mn in *Fagus/Carpinus* throughfall (TBH_{Mn}, mg m^{-2} yr^{-1}) is 123.1 and 99.5, respectively. These values should reflect both the input through atmospheric deposition, and through leaching/ion-exchange of the metabolic Mn.

Net metabolic throughfall (nTBH = TBH_{Mn} - D_{Mn}) equals canopy leaching if no atmospheric Mn is retained on the vegetation: nTBH$_{Mn}$ was 109.8 and 90.7 in 1995 and 1996, respectively. This clearly shows internal cycling of Mn dominates over inputs from bulk precipitation by almost a factor of 10. These values document the dominancy of the internal metabolic flux of Mn in the forested landscape. To compare the extent of this flux between deciduous and coniferous stands (conifers account for 53 % of the catchment area), sampling of throughfall below *Picea* stands began in May 1996. The plot of samplers was placed below a 30 year old stand. Comparison of the first 8 months of *Picea* throughfall sampling with that of *Fagus/Carpinus* throughfall shows that the former flux is 3.4 times higher.

Vertical distribution of Mn in soils is affected by its internal cycling. To assess the depth range of the intensive organic matter turnover and reach of the Mn - rich throughfall we have collected soil samples from six soil profiles in the *Fagus* stand. Seven distinct soil horizons were identified, and the fraction <1 mm was extracted with dilute HNO_3 to evaluate the amount of weakly bound Mn. The content of extractable Mn rapidly decreased with depth, with the uppermost (0 to 15 cm) horizon being more than four times higher in these forms of Mn, than in the deepest soil layers.

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