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SYNOPSIS

The relative importance of natural production of H⁺ in soil acidification

A. Breeuwsma and W. de Vries (Soil Survey Institute, Marijkeweg 11, 6709 PE Wageningen, Netherlands)

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Abstract. Soil acidification resulting from natural causes is quantified and compared with literature data on soil acidification induced by man via land use and acid rain.

Key-words: soil acidification, natural, anthropogenic, input-output balance, calcareous soils, podzolic soils, acid rain.

Introduction. Acid rain's contribution to soil acidification is controversial. Some authors state that acid rain is a major source of protons (Ulrich, 1983; Ulrich & Matzner, 1983) whereas others believe soil acidification mainly results from natural causes and land use (Rosenquist et al., 1980; Krug & Frink, 1983). This dissension arises partly because some authors have only considered parts of the element cycles relevant in soil acidification. In this paper the different acidification sources accounting for all the processes involved are compared quantitatively.

Natural soil acidification. Natural soil acidification mainly results from the dissocia-

tion of weak acids (de Vries & Breeuwsma, 1984). The acidification rate can be quantified by balancing input versus output for the relevant acid-producing anions (HCO_3^- and/or RCOO^-). Values thus obtained vary from 7.2-12.8 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$ for calcareous soils to 0.1-0.7 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$ for podzolic soils (Ulrich & Matzner, 1983; van Breemen et al., 1984). In calcareous soils, estimates can also be made by using the dissolution rate of CaCO_3 . Calculated values vary between 7.5-20 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$ for CO_2 pressures in the soil varying from 5 mbar (aerobic soil) to 100 mbar (maximum in anaerobic soil) and an excess precipitation of 300 mm yr^{-1} .

Another method of estimating the rate of natural acidification is by quantifying past decalcification and/or podzolization. This can be done by comparing the amount of weatherable cations in the topsoil with the amount in the presumed parent material. Furthermore, the time evolved since the process started has to be estimated. Such estimates have been made for calcareous soils in the Dollard polders in the Netherlands (Edelman & de Smet, 1951). The values obtained indicate an acid production of circa 8-15 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$.

Literature values on the natural acidification rate of soils most susceptible to acid rain, i.e. the non-calcareous sandy soils (usually podzolic soils in the Netherlands), are scarce. Therefore, we analysed the cationic composition of six soil profiles: a humic podzol, three gleyic podzols and two leptic podzols. The major elements (Al, Fe, Ca, Mg, Na, K) were measured after destruction with a mixture of HF, HCl and HNO_3 . The samples were all taken in non-agricultural land (forest and heath) where anthropogenic influence has been small. To enable the underlying parent material to be compared with the overlying podzolized material, corrections were made for the influence of biological activity which has led to an increase in the volume (thickness) of the topsoil and a decrease in the amount of weatherable cations per unit volume. This effect should not be ascribed to weathering. We assumed that the original density of the topsoil equalled that of the parent material. The original thickness was calculated by assuming that the product of thickness and density had not changed in time.

The acidification rates based on the net leaching of Al, Fe and bases (Ca, Mg, Na, K) varied between 0.1-0.9 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$, assuming that the podzolization started approximately 10 000 years ago.

The values for the natural acidification in calcareous and podzolic soils obtained by comparing topsoil and parent material agreed well with those obtained by balancing input versus output for bicarbonate and organic anions.

Anthropogenic acidification of soil. At present, soil acidification is strongly anthropogenically influenced via land use (removal of vegetation) and acid rain.

Vegetation removal leads to a continuous assimilation of a surplus of non-nitrogen cations over anions (de Vries & Breeuwsma, 1984). Data on this process, obtained by measuring growth rates and chemical composition of the vegetation, vary between circa 0.5-2.0 $\text{kmol H}^+ \text{ha}^{-1} \text{yr}^{-1}$ (Ulrich & Matzner, 1983; van Breemen et al., 1984). Another effect of clearing vegetation is that it can lead to a significant production of H^+ because of net mineralization (de Vries & Breeuwsma, 1984). In

a deforested ecosystem in Hubbard Brook, New Hampshire the acidification rate resulting from this process was $6.1 \text{ kmol H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ (van Breemen et al., 1984). In agricultural soils, where vegetation is removed far more frequently, the amount of lime that must be applied to maintain a favourable pH indicates that acid production resulting from this process ranges between $3\text{-}14 \text{ kmol H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$.

The mean potential input of acidic substances in soils in the Netherlands is $5.8 \text{ kmol H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ but in forests it can attain $7.5 \text{ kmol H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$. However, values for the actual acidification rate vary between $2.0\text{-}6.5 \text{ kmol H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ in Dutch forest soils (van Breemen et al., 1984).

Conclusion. A comparison between the acid production resulting from natural and anthropogenic sources of proton reveals that natural soil acidification is most important in calcareous soils, whereas land use largely determines the acidification of noncalcareous agricultural soils and acid rain that of non-calcareous, non-agricultural soils.

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