# PRINCIPAL GEOGRAPHIC VARIATION IN THE ACIDIFICATION OF **SWEDISH FOREST SOILS**

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Abstract. The principal geographic variation in acid-base status of 25 deep soil profiles (maximum 2.6 m deep) was investigated along three transects across Sweden. The transects represent gradients in the atmospheric deposition of acidifying compounds. A latent variable describing the acidity of the profile was extracted by Principal Component Analysis (PCA) and found to contain information that could be geographically interpreted. The variable was correlated more strongly with the atmospheric deposition of S ( $r = -0.86$ ) than with groundwater recharge ( $r = -0.30$ ) or base mineral index  $(r = 0.45)$ . It was concluded that variation in the deposition of S, in the form of H<sub>2</sub>SO<sub>4</sub>, is the main factor responsible for the large geographical differences in acidity in forest soils along transects from west to east in southern and middle parts of Sweden.

#### 1. **Introduction**

Soil acidification, defined as a decrease in the acid-neutralizing capacity of the soil (van Breemen *et al.,* 1983), is a natural soil-forming process in areas with humid climate. In an undisturbed ecosystem two processes are important: *biological acidification* caused mainly by the release of  $H<sup>+</sup>$  in connection with the uptake and accumulation of excess metal cations in biomass, and the *leaching of metal cations* together with bicarbonate ions and organic acid anions. However, in many parts of Europe and North America industrial activities, mainly the use of fossil fuels, have increased the concentration of  $H_2SO_4$  and  $HNO_3$  in the precipitation and pH has decreased from approximately 5.6 to below  $4.5$  (Odén, 1968; Reuss *et al.,* 1987). Since the bioaccumulation of N is usually very efficient, whereas S accumulates in the ecosystem to a much lesser extent, the deposition of  $H_2SO_4$  is generally the main factor enhancing soil acidification in all soils, except those with a high nitrification rate or high  $SO_4^2$ <sup>-</sup> adsorption capacity.

In a retrospective study made in old stands of Norway spruce *(Picea abies*  Karst.), Hallbäcken and Tamm (1986) showed that the effect of stand age on soil pH is substantial in the upper soil horizons but very small in the C horizon. This is in agreement with the theoretical assumption that biological acidification, since it provides few leachable anions, should be rather low below the rooting zone. Thus, when the aim is to geographically assess the influence of strong acid deposition on soil chemistry status, there would seem to be good reason to include chemical data from the soil below the rooting zone since it will be less influenced by biological acidification. Although data on the chemical status of soil samples from depths below 1 m are scarce, they do exist. Some of the data from the project described here have been presented earlier (Eriksson *et al.,* 1992), and there are also data



Fig. 1. Map of Sweden showing the location of the sampling sites along transects T1, T2 and T3.

available from areas where soil was sampled by drilling (Ulrich and Malessa, 1989).

Geographical variations in soil acidity due to acid deposition might be difficult to find since soil acidification is a complex process, that also depends on a number of factors unrelated to the magnitude of the deposition. Two variables that would be of importance below the root zone is the amount of water percolation through the profile and the mineralogy of the parent meterial.

The purpose of this study was to determine the soil acidification status in deep soil profiles along transects in Sweden and relate the data obtained to geographical differences in the deposition of S, the recharge of groundwater and the base mineral index of the soil.

## **2. Materials and Methods**

#### 2.1. SAMPLING SITES

All sampling sites were situated in temporary sampling plots used for forest productivity measurements during 1947-1963. The sampling sites were chosen along three transects, labelled T1, T2, and T3, representing the three geographical regions Götaland, Svealand and Norrland (Figure 1). T1 and T2 were oriented parallel to the prevailing wind direction. Each site was chosen to represent a recharge area for groundwater, i.e. an area with a high capacity for infiltration of rain and snowmelt. All sites had coniferous forest stands, and the soils were more or less podsolized. Twenty-four of the 25 soils were developed in glacial till and one was developed in a glacifluvial deposit. Soil types, classified according to Soil Taxonomy (USDA, 1981) are presented in Table I.

The total deposition of S, with a correction made based on the present type of forest stand, was estimated from deposition maps published by Lövblad et *al.* (1992). Groundwater recharge calculations were based on unpublished data provided by the Swedish Meteorological and Hydrological Institute (SMHI).

## **3. Soil sampling**

A large sampling pit, in the middle of the sampling plot, and four smaller pits, one in each comer of the plot, were dug by machine. Although the organic horizons were sampled and analyzed, their chemical properties are much different from the mineral soil and therefore not directly comparable with the mineral soil samples. Thus, only the mineral soil horizons are considered in this paper. Samples were collected down to 80 cm depth from top of the E horizon in the small pits and down to 260 cm in the large pit, when possible. The E horizon was sampled separately, and the top of the B horizon was sampled down to 10 or 20 cm depth depending on the thickness of the E horizon. The rest of the profile was sampled at fixed depths from the top of the E horizon. Layers of 10 cm thickness were used down to 80 cm depth, while layers of 20 cm thickness were used from 80 cm down to 260 cm depth. Samples from the five pits on each site were pooled to obtain representative samples in the top of the profile, where spatial variability is high.

In the laboratory the soil samples were sifted through a 2 mm sieve, and part of each sample was airdried at 40 °C. Remaining soil material was kept moist at 1 to  $2^{\circ}$ C prior to analysis.

## 3.1. SOIL CHEMICAL ANALYSIS

pH was determined in the field on fresh, unsieved soil measured in an equilibrium solution with deionized water and a soil:solution ratio of 1:2 (V:V). The pH measurement was made with a glass electrode on a Hanna HI 8424 pH meter. Samples were allowed to equilibrate overnight before measurement.

## 356 E. KARLTUN



Background data concerning the profiles used in the study



 $\degree$  Soil classification according to USDA (1981).

 $<sup>b</sup>$  Maximum sampling depth.</sup>

- c S deposition from LOvblad *et al.* (1992).
- $d$  Groundwater recharge is calculated from data provided by SMHI.

 $e$  Base mineral index according to Tamm (1934).

Exchangeable acidity and base cation determinations were made on air-dried samples. Exchangeable acidity was determined by the titration method described by Yuan (1963) using 1 M KC1 as extractant and titrating to pH 7 with 0.01 M NaOH. Base cations were extracted by leaching with 1 M NH4C1, and Ca, Mg, K and Na content was determined on an atomic adsorption spectrophotometer (AAS). Every fifth sample was run in duplicate.

The concentration of  $SO_4^2$  was determined in an equilibrium solution with deionized water and a fresh soil sample. A 12.50 g portion of soil and 25 mL of deionized water were shaken together for 15 min  $hr^{-1}$  overnight. The sample was centrifuged for 10 min at 9000 rpm, and the pH of the supernatant was measured with a glass electrode on a Radiometer PHM 84 research pH meter. A portion of the supernatant was filtered through a  $0.2 \mu$ m Microgon membrane filter and analyzed for  $SO_4^2$ <sup>-</sup> on a Dionex 2000i ion chromatograph equipped with as AS5 anion analytical column and a conductivity detector. All samples were run in duplicate.

The base mineral index (BMI) is defined as the percentage of minerals in the sand fraction between 0.5 and 0.25 mm in diameter with a density equal to or higher than 2680 kg  $\text{m}^{-3}$ . This is a reasonably fast method for estimating the content of heavy minerals in the parent material and was first introduced by Tamm (1934). The sand fraction was air-dried at 105 °C. A 1.00 g portion of the sample was transferred to a separation funnel. Thoulet's solution, a salt solution of KI and  $HgI<sub>2</sub>$ with a known density of 2680 kg  $\text{m}^{-3}$ , was added, and sample and liquid were mixed by gentle agitation. After agitation, the separation funnel was gently stirred to suspend the minerals attached to the glass surfaces. After 30 min the heavier fraction was removed and washed five times with deionized water. Thereafter the heavy fraction was air-dried at  $105^{\circ}$ C and weighed.

#### 3.2. DATA ANALYSIS

Conventional univariate and bivariate statistical methods have limited capabilities in describing complex systems. They require that the variables are normally distributed, a precondition that is more often assumed than tested, and that they are independent. The conventional multivariate methods (e.g multiple regression) are restricted to data matrices which have more objects than variables and are based on the assumption that the variables are independent.

Principal Component Analysis (PCA) (see Wold *et al.,* 1984) provides a useful statistical tool for performing explorative data analysis. It is not restricted by assumptions of normally distributed data or independence of variables. With PCA one can easily reduce large data set into intepretable figures, especially if there are many variables. It has proven very useful when interpreting complex biological and chemical systems (Hämäläinen, 1991).

A Principal Component (PC) is a least-squares regression through a multidimensional space spanned by the original variables. The first PC extracted from a data set describes the direction of the largest variation in the data set. The second PC describes the direction of the largest remaining variation, etc. The PCs are always perpendicular to each other. When two or more PCs are computed the objects can be plotted in a coordinate system defined by the PCs, i.e., a *score* plot. The variables can also be plotted in the same coordinate system but in the object space, i.e a *loading* plot.

The data in the study were arranged in a  $25 \times 126$  matrix with the 25 soil profiles as objects and the measured chemical variables at every specific depth



Fig. 2. Loadings plot for all variables in the coordinate system defined by PC1 and PC2. The distance from the origin is an indication of the influence of each variable on PC1 and PC2, respectively.

as variables. For example, pH between 20 to 30 cm depth became one variable and pH at 30 to 40 cm another. Thus, the soil chemical data for each object formed a characteristic 'profile' describing the vertical gradients of the measured soil chemical characteristics. All the soil chemistry variables used in the PC model were intensity variables, i.e., they were expressed as an activity (pH), concentration (p[SO<sub>4</sub>]), or percentage (Al, Ca, Mg, K, Na as % of CEC<sub>e</sub> and not as an amount per unit weight of the soil sample.

PCA was carried out to reduce the large data set to one latent variable that would describe the acidity status of the soil profiles. By scaling each variable, through multiplying the data in each column with the inverse of the column standard deviation, the variance for each variable was set to 1 (Wold *et al.,* 1987), i.e. each variable had an equal opportunity to influence the statistical analysis despite their different numerical magnitudes. The data set was centered by subtracting the column averages (Wold *et al.,* 1987). The latent variable obtained was then compared with the geopgraphic location and tested for correlation with data on S deposition as well as the amount of groundwater recharge and the base mineral index of the soil.

## **4. Results and Discussion**

Two Principal Components (PCs) were extracted: The first explained 34.5% of the variance in the data set and the second explained 16.6%. In Figure 2, loadings for all variables are plotted in the coordinate system defined by PC1 and PC2. To simplify the interpretation of the figure, the different depth notations are not included. Thus, all the pH variables in the plot have the same symbol. Variables believed to be affected by the acidity of the soil sample (pH, Al, Ca, Mg, p[ $SO_4$ ]) are clearly separated from the origin, mainly along PC1, whereas variables less dependent on acidity (K, Na) mainly influence PC2. Compared with PC2, PC1 explained more of the information in the variables sensitive to acidity. Wold *et al.*  (1987) pointed out that the first sets of scores can be seen as latent variables that describe most of the information in the data. In this case PC1 mainly describes the direction of acidity of the profiles. The scores for the 25 profiles along the first PC could thus be used as a latent variable describing their acidity status.

If the acidity status changes along the east-west transect, i.e., along the deposition gradient, the scores of the first PC would contain information that could be interpreted geographically. In Figure 3A the profiles are plotted with their latitude along the y-axis and longitude along the x-axis. In Figure 3B the longtitude is replaced by the scores of the first PC. It is evident that the scores along the first PC, based solely on soil chemical data, contain information that can be attributed to the geographical locality of the profile along the transect. The score range is wider along T1 than along T2, whereas there is little variation along T3. This pattern is consistent with the range and magnitude in the deposition gradients (Table I). Despite the high deposition in the area, profile no. 2 seems to be less affected, probably owing to the limited sampling depth at that site (80 cm) due to a high groundwater table. The important data from the deeper horizons are missing. On these grounds, profile no. 2 was considered an outlier and was omitted from further statistical analysis. The perceptible difference in scores between profiles no. 3 and 4 despite their geographic closeness is interesting. It may be an effect related to the differences in stand composition and structure between sites, leading to differences in the amount of dry deposition. The forest at site no. 3 is a dense Norway spruce stand receiving a large amount of S as dry deposition whereas site no. 4 supports an open Scots pine stand receiving less S as dry deposition (Lövblad *et al.*, 1992). The latent variable for the acidity was correlated with S deposition, groundwater recharge and the BMI of the profiles (Figures 4A-C). S deposition showed the best correlation ( $r = -0.86$ ), whereas the correlation to groundwater recharge ( $r = -0.30$ ) and BMI  $(r = 0.45)$  were rather poor. These results confirm that it is the amount of acid deposition in the form of  $H_2SO_4$  that is responsible for the large geographic differences in soil acidity between the western and eastern parts of Sweden. Furthermore, it can be concluded that in high-deposition areas primary minerals are not weathered fast enough to neutralize the acid input even if the till is several meters thick.



Fig. 3. (A) Latitude vs longitude for all sampling sites. (B) Latitude vs scores (PC1) for all objects. Figures refer to site hr.



Fig. 4. S-deposition (A), groundwater recharge (B) and base mineral index (C) plotted against scores of PC1.

#### 362 E. KARLTUN

## **5. Conclusions**

It was concluded that:

- there is large geographical variation, even at greater depths, in the acidity of forest soils along transects from west to east in southern and middle parts of Sweden
- the major factor contributing to these differences is variation in the deposition of S in the form of  $H_2SO_4$
- primary minerals do not weather fast enough to neutralize the acid input in high deposition areas

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