

## **Tools for prediction of the acidification of aquifers in sedimentary rocks (Wingst area, northern Germany)**

**FRIDO REINSTORF, WOLFGANG WALTHER,  
KERSTIN HEBLACK & THOMAS CRAMER**

*Dresden University of Technology, Institute for Groundwater Management, D-01062 Dresden, Germany*

e-mail: [frido.reinstorf@mailbox.tu-dresden.de](mailto:frido.reinstorf@mailbox.tu-dresden.de)

**Abstract** Results of a recent research project carried out in a sedimentary rock aquifer in northern Germany are presented. The paper deals with various methods of identification of the status and prediction of subsurface acidification processes. For the identification of the status, laboratory methods, e.g. elution methods using drilling core material, and evaluation methods determining the chemical characteristics of the soil solution, were tested. For prediction tasks, mathematical models for mass balances, e.g. AcidProgress, and process description, e.g. SAFE, were tested and evaluated. With the aid of the process-oriented models, a prediction of the future status, e.g. a period of 140 years, can be computed given a future deposition scenario. The methods presented are suitable for decision making and problem management.

**Key words** acidification; acidification model; acidification prediction; management tools

### **INTRODUCTION**

Western European aquifers often have been contaminated for many years with non-point source pollution by airborne substances. The important airborne substances include the strong acids of nitrate and sulphate, and organic substances. Because the acidic atmospheric deposition is buffered by reactions in soils, metals, mainly cations, are mobilized. The mobilization of metals is caused by the exchange of  $M_b$  cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) with hydrogen ions ( $H^+$ ). Over many years, the cations are transported to the groundwater. In many regions of Germany, the acidification front migrates downward slowly. In some cases, the front has already reached the groundwater. The acidification of groundwater needs to be managed, particularly in groundwater protection areas. Several methods can be applied to retard or stop the migration of the acidification front to the groundwater, e.g. treatment of the soil with lime, changes in the kind of land use. Nevertheless, the main objective of preservation strategies should be the reduction of the deposition of strong acids. In addition to providing remediation strategies, science should provide reliable methods for identifying the location of the acidification front and models for predicting the migration. In particular, there is a lack of practical methods which can be used by management authorities and water engineers to make decisions. In the "Acidification of the Wingst Area (Northern Germany)" research project, several models and methods were applied and verified.

## DEFINITION OF ACIDIFICATION AND BUFFERING REACTION

Acidification of the solid phase is the long-term decrease of the acid neutralization capacity (*ANC*). The *ANC* can be measured as an increase of acidity (*Aci*) in the whole system (Sigg & Stumm, 1994):

$$Aci = 2[SO_4^{2-}] + [Cl^-] + [NO_3^-] + \dots - [Na^+] - [K^+] - 2[Ca^{2+}] - 2[Mg^{2+}] \quad (1)$$

In addition to buffering by the phase-interior process in the fluid phase (soil water and groundwater), the acid buffering occurs mainly by interactions between the fluid and the solid phase (soil water/groundwater  $\leftrightarrow$  solid phase). Both the weathering and the cation exchange properties of the solid phase are relevant to these processes. The most important parameter determining the size of the buffer is the base saturation (*BS*). The larger the *BS* the larger the acid amount that can be buffered without significant changes of pH. The base saturation is defined as:

$$BS = \frac{\sum (Ca^{2+} + Mg^{2+} + Na^+ + K^+)}{CEC_{eff}} \cdot 100 \quad (2)$$

where:

$CEC_{eff}$  = effective cation exchange capacity

$$= \sum \text{ion - equivalents} = \sum \frac{n_i \cdot i^{z_i}}{z_i} \div m$$

in  $\mu\text{moleq g}^{-1}$ ;  $n_i$  = mols of cation  $i$  to be exchanged [-],  $z_i$  = valence of the cation  $i$  [-],  $m$  = weight basis [g].

The silicate and exchange buffer is particularly important for quantification of buffering capacity. The acid buffering capacity decreases rapidly at less than 80% *BS*. A soil, therefore, is acidified if  $M_b$  - cations  $\leq$  80% of  $CEC_{eff}$  and the pH ( $CaCl_2$ )  $\leq$  5 (Ulrich & Malessa, et al., 1989). An example of the chemical characteristics of a local acidification front is shown in Fig. 1.

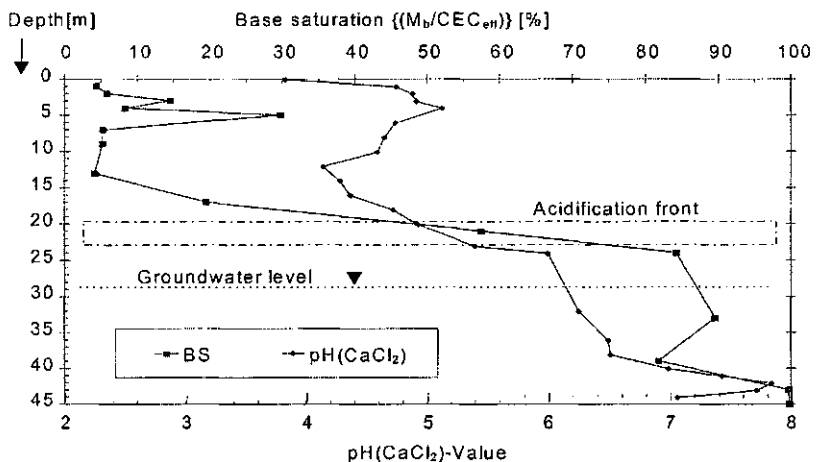


Fig. 1 An example of the chemical characteristics, specifically the base saturation and pH, of a local acidification front.

## METHODS FOR ESTIMATION OF THE ACIDIFICATION STATUS

Methods are presented for evaluation of the acidification status of the solid phase with respect to definition of the buffer regions and reactions, e.g. Ulrich (1981). In addition to hydraulic parameters, e.g. hydraulic conductivity, and values characteristic of the soil substrate, e.g. bulk density, the important information must be determined by investigations on drilling material. In particular, the chemical composition and buffering capacity of the subsurface material should be investigated using at least two methods (after Meiwes *et al.*, 1994): pH (CaCl<sub>2</sub>) and titrimetric determination of the buffer curve with  $\text{pH} = f(\text{Aci})$  and  $\text{pH} = f(\text{Alk})$ .

The *ANC*, an important parameter, can be estimated with this methods and other important parameters, e.g. *BS*, can be computed too. The *ANC* and *BS* determinations aid the assessment of the acid–base status of the solid phase.

## METHODS FOR DETERMINATION OF THE MIGRATION OF THE ACIDIFICATION FRONT

Recent acidification models can be divided into two groups: mass-balance models and process-oriented models. Mass-balance models focus on estimating inputs, outputs and changes in storage, but do not rely on knowledge of the internal processes. Mass-balance models are suitable for estimating medium-term (decades) and long-term (more than 100 years) trends and have relatively small demands on data. An example of a mass-balance model is AcidProgress (Malessa *et al.*, 1997) which estimates the timing of changes in the base cation status of the unsaturated zone. The model calculates the balance between the acid load and *ANC*. Table 1 shows an example of an estimate of the duration of base exhaustion over a vertical distance to the saturated zone using AcidProgress. The computed duration of the exhaustion of the base reservoir is 270 years for the vertical profile of 7 m depth.

**Table 1** An example of the calculation scheme with input parameters and results for the AcidProgress model.

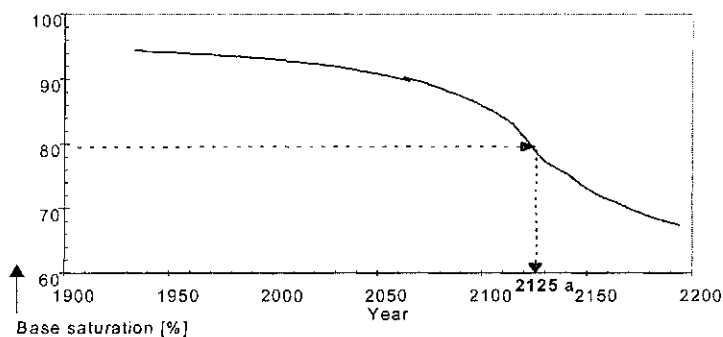
Parameters	Unit	Value
Thickness of the weathering layer ( <i>MV</i> )	m	29
Depth of the acidification front ( <i>Vfr</i> )	m	22
Remaining range ( <i>VS</i> )	m	7
Base reservoir ( <i>BV</i> )	kmol <sub>eq</sub> ha <sup>-1</sup>	528
Acidic load ( <i>SI</i> )	kmol <sub>eq</sub> ha <sup>-1</sup> .year <sup>-1</sup>	2.0
Silicate weathering	kmol <sub>eq</sub> ha <sup>-1</sup> .year <sup>-1</sup>	0.05
Effective acid load ( <i>SI<sub>eff</sub></i> )	kmol <sub>eq</sub> ha <sup>-1</sup> .year <sup>-1</sup>	1.95
Duration of exhaustion of base reservoir ( <i>DA</i> )	year	270

The physico-chemical laws describing soil inorganic chemical processes, e.g. acid–base reactions and redox reactions, are the basis of process-oriented models; they can address short-term, medium-term, and long-term trends. An example of a process-oriented model is SAFE (Sverdrup *et al.*, 1995). The model calculates the chemical composition of the soil water for various soil layers and time steps as affected by the atmospheric deposition and local soil chemical parameters. Table 2 shows an example

of a simulation using SAFE. For this example, Table 2 lists the chemical composition of the soil water to a depth of 29 m (the position of the groundwater level) in the year 2090 for the case of constant acidic atmospheric deposition. The model simulates the concentration of several substances in the soil water and the sum parameter. The model also computes the velocity of the acidification front migration, which is approximately 3 m in 100 years. Figure 2 shows the temporal change in *BS* at a depth of 29 m. The model predicts that the acidification front will arrive at a depth of 29 m in 125 years.

**Table 2** An example of simulated soil water solute concentrations through a depth of 29 m in the year 2090 using the SAFE model.

Depth (m)	pH	ANC ( $\mu\text{eq l}^{-1}$ )	Ca ( $\mu\text{eq l}^{-1}$ )	Weath. ( $\text{keq l}^{-1} \text{ha}^{-1} \text{year}^{-1}$ )	Mb/Al	N ( $\mu\text{eq l}^{-1}$ )	SO <sub>4</sub> ( $\mu\text{eq l}^{-1}$ )	Cl ( $\mu\text{eq l}^{-1}$ )	Na ( $\mu\text{eq l}^{-1}$ )	Al ( $\mu\text{eq l}^{-1}$ )
0.2	3.4	-561	117	0.0	0.4	357	273	257	209	457
0.8	3.7	-877	150	0.0	0.3	525	422	446	366	735
2.0	4.3	-609	222	0.1	0.3	550	425	447	366	630
6.0	4.2	-538	295	0.3	0.4	545	427	447	367	627
15.0	4.8	-573	367	0.4	0.5	540	430	448	368	559
22.0	5.0	-481	495	0.5	0.6	538	436	451	370	567
24.0	5.2	-390	624	0.8	0.8	534	439	452	371	522
27.0	5.9	-298	752	3.2	1.2	553	489	452	421	663
29.0	6.9	-23	1657	4.2	4.2	580	561	456	478	0



**Fig. 2** SAFE model simulation of the temporal variations in *BS* at a depth of 29 m (groundwater level).

## CONCLUSIONS AND OUTLOOK

In some regions of northern Germany acidification fronts have migrated to considerable depths. Zones of some aquifers have already been acidified. The modelling results provide some preliminary results for predicting the migration of the acidification front. These predictions contribute valuable information for determining suitable recommendations for action.

There are several tools and methods for estimation of the acidification risk. In addition, short-term and locally suitable counter measures (quick fixes) are known, but the long-term and sustainable management strategies are not known.

Therefore, the aim of the research was to verify model tools and methods for a catchment containing a drinking water supply. The models and methods presented were selected from several available tools. Having tested them, we recommend that they be used as management tools. The transferability of these tools, the models and methods, to other geographical areas, is being tested at another place in northern Germany.

**Acknowledgement** The authors thank the Ecology Agency of Lower Saxony, Germany for funding this research project.

## REFERENCES

- Malessa, V. (1997) Umsetzung von Forschungsergebnissen in Planungs- und Entscheidungsverfahren. *Niedersächsisches Landesamt f. Bodenforschung, Hannover: Arbeitshefte Boden* 3.
- Meiwes, K. J., Merino, A. & Fortmann (1994) Untersuchung der Versauerung in Bohrprofilen von Meßstellen des Grundwassergütemeßnetzes (GÜN) des Landes Niedersachsen. *Berichte des Forschungszentrums Waldökosysteme /Waldsterben*, Göttingen Reihe B 34, 86 S.
- Sigg, L. & Stumm, W. (1994) *Aquatische Chemie: Eine Einführung in die Chemie wässriger Lösungen und natürlicher Gewässer* (3 Aufl.). VDF-Verlag, Zurich, Switzerland.
- Sverdrup, H., Warfvinge, P., Blake, L. & Goulding, K. (1995) Modelling recent and historic soil data from the Rothamsted Experimental Station, UK, using SAFE. *Agric. Ecosys. Environ.* 53, 161–177.
- Ulrich, B. (1981) Ökologische Gruppierung von Böden nach ihrem chemischen Bodenzustand. *Z. Pflanzenern. Bodenk.* 144, 289–305.
- Ulrich, B. & Malessa, V. (1989) Tiefengradienten der Bodenversauerung. *Z. Pflanzenern. Bodenk.* 152, 81–84.