CHAPTER 4

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Mapping Groundwater Sensitivity to Acidification in Europe

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4.1. Introduction

Acid deposition alters the properties of topsoil and the composition of the fluxes in forested soil-water systems. Recent changes in the chemical properties of soils and surface waters in small watersheds have been reported in northern Europe and in the northeastern United States (e.g., Likens et al., 1977; Wright et al., 1980b). Nutrient cycling in soil appears to be disturbed, and mobilization of metals from mineral structure seems to accelerate in certain areas owing to acidic precipitation (e.g., Norton et al., 1980; Ulrich, 1983b). Ultimately, these changes may affect the chemical composition of groundwater.

Historical records of groundwater quality are scarce. However, recent monitoring of groundwater chemistry has uncovered changes occurring in some shallow, noncalcareous, sandy aquifers. An increased content of leached base cations and sulfate, accompanied by a decrease in bicarbonate, has been documented by Jacks et al. (1984) in parts of Sweden, by Soveri (1985) in Finland, and by Wieting (1986) in the Federal Republic of Germany.

Groundwater is an important source of Europe's water supply. The proportion of drinking water extracted from groundwater ranges from 30% to 70% in most of Europe. Denmark, which uses only groundwater, and Norway, where less than 10% of the waterworks use groundwater, form exceptions. A high sulfate-to-bicarbonate ratio in groundwater extracted from private wells causes the corrosion of supply pipes, which becomes an economic issue in regions with many private wells. Acidic drinking water may also dissolve copper from the pipes.

At the International Institute for Applied Systems Analysis (IIASA), a methodology has been developed for evaluating the sensitivity of European aquifers under forested soil to the deposition of acidifying compounds originating from transboundary atmospheric pollutants. This chapter presents maps of aquifer sensitivity and risk resulting from the application of this methodology on a European regional scale.

4.2. Impact of Acid Decomposition on Aquifer Systems

The impact of acid deposition on the aquifer is determined by the neutralizing properties of the overlying soil and that of the aquifer itself. Cation exchange and mineral weathering are the primary transformation processes that contribute to the neutralization of acid deposition. Hydrogen ions in the matric water participate in cation exchange at the surface of the soil solids, thereby causing the leaching of base cations. The pool of exchangeable base cations is replenished by the weathering of minerals.

Ions in precipitation affect the matric water concentrations. The rates of the soil-forming processes, such as cation exchange, weathering, nutrient mineralization and assimilation, depend on the concentrations of ions in the matric water. If the atmospheric input of hydrogen ions changes over time, the rates of the soil processes change. In the short run (years), this will influence the concentrations of the matric water. In the long run (decades), the changing composition of the matric water is expected to induce changes in the properties of the solid phase of the soil and the composition of groundwater.

The concentrations of elements in groundwater depend on the chemical composition of the recharge from the unsaturated zone, on the mineral composition and the weathering rate in the saturated zone, and on the residence time of groundwater.

The composition of the recharge to groundwater is influenced by the residence time of the water in the unsaturated zone. The ion exchange reactions are almost instantaneous; but the longer the time available for contact between the matric water and the mineral surfaces, the higher the content of weathered cations (calcium, magnesium, potassium, and aluminum) in the recharge to groundwater. The residence time in the unsaturated zone increases with the depth and decreases with the permeability of the soil. Furthermore, the mineral composition of the soil and the organic matter content influence the recharge composition, through their impact on the rates of ion exchange and weathering.

The weathering rate and the chemical composition of the minerals in the saturated zone determine the alkalinity production rate within the aquifer. Calcareous bedrock is easily weathered, whereas silicate bedrock weathers slowly. In the weathering reactions of silicate minerals, base cations and aluminum ions are released and bicarbonate ions are formed. The rate of alkalinity production in noncarbonate soil material of granitic origin has been estimated in the range of 1 to 40 meq m $^{-3}$ a $^{-1}$ (Nilsson, 1986).

The residence time of the groundwater in reservoirs determines the time available for the weathering reactions. The residence time of groundwater is

determined by the rates of recharge, discharge, and extraction, as well as by the size of the aquifer. The climatic regime influences the rate of recharge through the rate of precipitation and the variables of temperature and vegetation, which together affect the rate of evapotranspiration. If there is no surface runoff, the rate of recharge can be approximated by precipitation minus evapotranspiration. The rate of recharge increases also with the hydraulic conductivity of the soil, which depends on soil texture and water content. The rates of recharge and discharge, furthermore, depend on the relief of the region, on the physical location of the aquifer, and on whether it is confined or unconfined.

4.3. Assessing the Impact on a Regional Scale

Few countries in Europe monitor environmental response to diffuse pollution. Data from regional monitoring of several environmental variables would obviously be the logical starting point for any appropriate assessment of regional acidification. Efforts have been made to intensify the regional surveillance of air quality and forest health. Few networks, however, have been established to monitor soil and groundwater quality on a national level, much less on the regional level. Sweden is an exception; a national network for monitoring groundwater quality was established there in 1968.

The lack of data regarding present and past chemical characteristics of soils and aquifers in Europe complicates the assessment of future acidification. Despite the empirical shortcomings, an evaluation has to be made. There are basically two possible approaches.

First, the geochemical processes that determine the impact of acid deposition on soils and aquifers may be described in a structural simulation model. The mechanisms of the neutralizing processes are mostly well known, and the main modeling problems lie in the complexity of the groundwater system and in the quantification of the process rates. The structural models are expressed as differential equations, describing the change per unit time in the state variables, or as algebraic equations, describing equilibrium reactions. A structural model of soil acidification on a regional scale has been developed by Kauppi et al. (1986). Extending Kauppi's soil model or an alternative structural model of the neutralizing processes in the unsaturated zone to include the dynamics of the saturated zone would require a complex hydrological model to account for the seasonal and regional variations in European hydrology. In addition, quantitative estimates of elemental transport, release, and accumulation in the unsaturated zone below the rooting zone are not available on a regional scale.

The second approach to assessing the impact of acid deposition on aquifer systems is to evaluate the regional potential for acidification on the basis of sensitivity analysis. An ecological system responds to its environment by variations in certain state variables, incited by changes in some driving functions. Apart from the driving functions, certain physical system characteristics, or sensitivity indicators, determine the amplitude of the response and the response time of the system.

If a system reacts very slowly to the driving functions, i.e., if the system is highly inert, changes that occur in the state variables are only slowly reversible. In assessing the anthropogenic impact on ecological systems, both the sensitivity and the inertia of the systems should be taken into account. In the long run, a highly sensitive system is worse off if it is also very inert, whereas a quickly reacting system may represent the worst case in the short run. The best case with respect to environmental damage is an inert system with low sensitivity to changes in the driving functions.

4.4. Assessment Method

In indicator or sensitivity analysis, the basic geochemical and physical characteristics that influence the chemical behavior of soil, groundwater, and surface waters are lumped into a number of indicators. The indicators are discrete variables that correspond either to a classification of the original continuous physical characteristics, such as soil depth and texture, or to a derived entity, such as neutralizing capacity. An indicator reflects certain properties that contribute to the overall sensitivity of the system. The overall sensitivity is obtained by aggregating the individual indicators.

The aggregation may be done, for example, by computing the weighted average of the individual indicators. Jacks and Knutsson (1982) followed this approach in evaluating the sensitivity of Swedish soil and groundwater to acidification. The disadvantage of the linear model is that the determination of the constant weighting coefficients is difficult. The mineral weathering rate, for instance, is an exponential rather than a linear function of the chemical composition of the minerals.

The difficulty of constant weathering coefficients can be overcome by using piecewise linear functions, which allow for the coefficients to vary with the indicators. Piecewise linear functions can be implemented by two-dimensional matrices for the stepwise aggregation of pairs of indicators. A method for evaluating the sensitivity of European groundwater to acidification, using aggregation matrices, was developed at IIASA (Holmberg et al., 1987). Carter and co-workers (1987) used a similar method for mapping the vulnerability of groundwater to pollution from agriculture.

4.5. Sensitivity Indicators

In our methodology, the neutralization capability is assessed on the basis of soil depth, texture, and base cation content; the size and the mineral composition of the aquifer; and the annual amount of water potentially available for recharge (Figure 4.1). The choice of these indicators was based on knowledge of the geochemical processes involved in neutralizing acid deposition and on the availability of data. The choice was also influenced by sensitivity studies conducted by Jacks et al. (1984), Aust (1983), and Edmunds and Kinniburgh (1986a). Data availability was a major consideration because of the regional scale of this model;

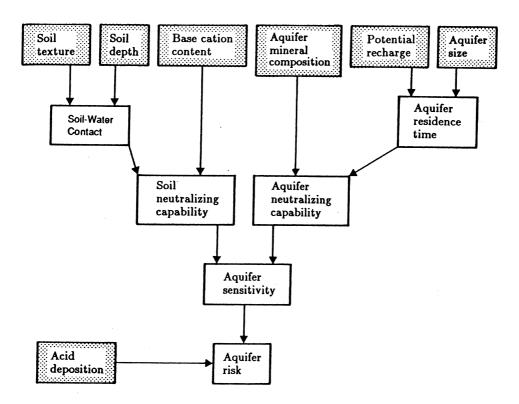


Figure 4.1. Aquifer sensitivity is assessed as the combined neutralizing capability of the aquifer and the overlying soil.

few sources of data are consistent over large areas, yet detailed enough for this purpose. Soil depth, texture, and base cation content were compiled from the Food and Agriculture Organization (FAO) Soil Map of the World (1974). Aquifer size and mineral composition were taken from the International Hydrological Map of Europe currently being compiled (UAH-UNESCO, 1970–1985).

The efficiency of neutralization by cation exchange in the soil depends upon the exchanging surface available for contact with the matric water. This factor is introduced through an indicator called soil-water contact, the value of which is determined on the basis of soil depth and soil texture. Soil texture is divided into five classes, ranging from coarse to fine. Soil depths are classified as either shallow or deep (less than or greater than 0.5 m, as defined in the soil types of the FAO soil map).

soil-water content =
$$f_1$$
 (depth, texture) . (4.1)

The resulting indicator soil-water contact, is assigned the rating poor (1), moderate (2), or good (3).

The total neutralizing capability of the soil is evaluated from the soil-water contact and the content of base cations in the top 0.5 m of soil. The base cation content was calculated from data on cation exchange capacity and percentage of base saturation for 80 European soil types. The indicator was divided into six classes: class 1 < 100 keq/ha, class $2\ 100-200$, class $3\ 200-400$, class $4\ 400-800$, class $5\ 800-1,600$, and class 6 > 1,600 keq/ha. We assume that the base cation content reflects the weatherability of the minerals in the unsaturated zone:

soil-neutr. capability =
$$f_2$$
 (soil-water contact, base cation content). (4.2)

The neutralizing capability of the soil is assigned the rating poor (1), moderate (2), or good (3).

Rather than create a comprehensive hydrological model of Europe, potential annual recharge, defined as annual precipitation minus annual evapotranspiration, has been chosen to account for the climatic impact. The potential recharge is divided into three classes: (1) > 400 mm, (2) 400-100 mm, and (3) < 100 mm. The International Hydrological Map of Europe defines four aquifer productivity classes based on permeability and aquifer size. This makes the estimation of residence time difficult. High productivity results from high permeability in extensive aquifers. However, low productivity may be caused by low permeability, small discontinuous water-bearing formations, or both conditions.

For the purpose of assessing aquifer sensitivity, highly productive aquifers were assumed to possess long residence times because of their sizes and depths. Low or nonproductive aquifers were assigned shorter times because groundwater moves primarily through fractures in these aquifers. The main aquifer of an area, given by the hydrogeological map, is considered. This implies that different types of aquifers are encountered – open as well as confined, and rock aquifers as well as aquifers in unconsolidated material. The aquifers were classified into four size categories ranging from small (1) to extensive (4). The potential recharge combined with the aquifer size gives an estimate of the residence time:

aquifer residence time =
$$f_3$$
 (potential recharge, aquifer size). (4.3)

The resulting residence time of the aquifer is classified in three classes from short (1) to long (3). The residence time is, on the other hand, also a measure of how easily any changes in the chemical composition may be reversed.

Aquifers have been classified into four mineral composition categories according to their mineral weathering rates. Class 1 contains acid or intermediate silicate rocks, sandstones, sands, gravels, and silts (i.e., no easily weatherable materials). Class 2 includes clays, claystones, slates, shales, graywackes, phyllites, and undefined silicate rocks. Class 3 contains the basic silicate rocks. Class 4 includes carbonate rocks such as limestone, dolomite, and marl (i.e., easily weatherable materials). The neutralizing capability of the aquifer was evaluated on the basis of the residence time of the groundwater and on the weatherability of the minerals in the aquifer:

aquifer-neutr. capability = f_4 (residence time, mineral composition). (4.4)

Finally, the sensitivity of the aquifer is evaluated as the inverse of the combined neutralizing capability of the soil and the aquifer. The sensitivity may in turn be combined with an estimate of regional deposition to yield the risk of groundwater acidification. The resulting sensitivity and risk values are ranked into three classes, ranging from the rating 1 for low to 3 for high sensitivity or risk (Figure 4.2).

4.6. Sensitivity

In the computer implementation of this methodology, Europe is subdivided by a grid system with individual cells of 1.0 degree longitude by 0.5 degree latitude. Data for each of the 1,844 grid cells are passed through the assessment algorithm and assigned a sensitivity class.

The resulting sensitivity class assignments can be mapped as shown in Figure 4.3. This map is based on the indicator data for the dominant (largest area) soil type and aquifer in each grid cell. It contains 528 grid cells of class 1 (low), 815 cells of class 2 (medium), and 501 cells of class 3 (high) sensitivity. As can be seen, nearly all of the aquifers in the Nordic countries are categorized as highly sensitive. Other regions of high sensitivity include northern Scotland, northwestern Spain, and parts of Central Europe.

4.7. Risk

This process can be carried one step further to assess aquifer risk – a combination of aquifer sensitivity and acid deposition. Regions with little ability to resist acidification (highly sensitive) and exposed to the highest degree of deposition carry the greatest risk of change. Conversely, those areas with large buffering capabilities and/or not subject to significant acid deposition carry little risk of change.

A sample risk map is shown in Figure 4.4. This map results from combining the sensitivity map in Figure 4.3 with the estimated 1980 sulfur deposition pattern (Alcamo et al., 1985). The deposition has been divided into three classes for this purpose $(0-1, 1-5, \text{ and } > 5 \text{ g m}^{-2}\text{a}^{-1})$. As can be seen, the majority of the aquifers at risk lie in Central Europe, the Nordic countries, the United Kingdom, and northern Italy. For some parts of the Continent, the Hydrogeological Map of Europe is not yet available. These areas are left unshaded in the maps.

In interpreting these maps, it is important to realize that intensive fertilization in some agricultural areas contributes more to groundwater acidification than transboundary atmospheric pollutants. For this reason, the results of this method are strictly applicable only to uncultivated areas, such as forests. Consequently, soil-neutralizing capability was evaluated on the basis of geochemical data for forest soils. Nevertheless, the same technique could be expanded to

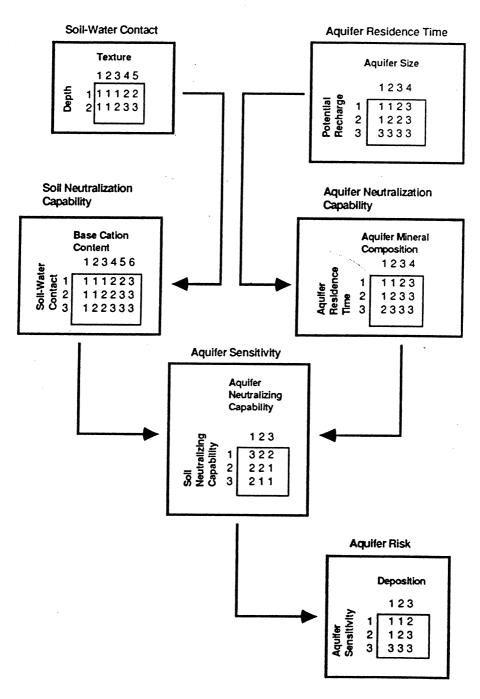


Figure 4.2. Aquifer sensitivity is assessed using combination matrices. The rating 1 stands for low and 3 for high neutralizing capability, sensitivity, or risk.

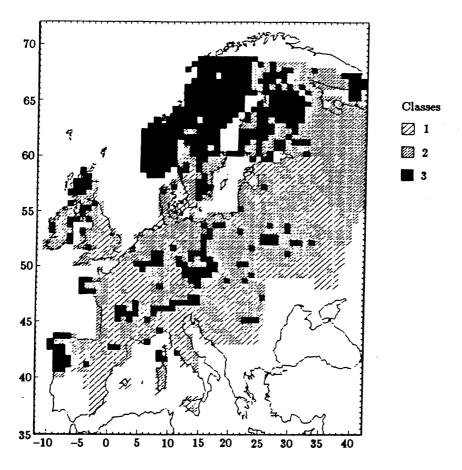


Figure 4.3. Aquifer sensitivity to acidification. The lightest shading stands for low sensitivity, while the darkest stands for high sensitivity, evaluated from the areally dominant indicators.

include agricultural soils. In that case, the risk would be evaluated by combining aquifer sensitivity with indicators representing land use and atmospheric deposition.

4.8. Uncertainty

Examination of the assessment technique and output variations under different input conditions suggests three sources of uncertainty: the input data, the function tables, and the spatial resolution of the data. There is no denying that the realities of regional environmental databases have forced some compromise in how the input data are included in the assessment technique. The indirect method for estimating aquifer size has already been described. Potential recharge may or may not be a good substitute for actual recharge because the

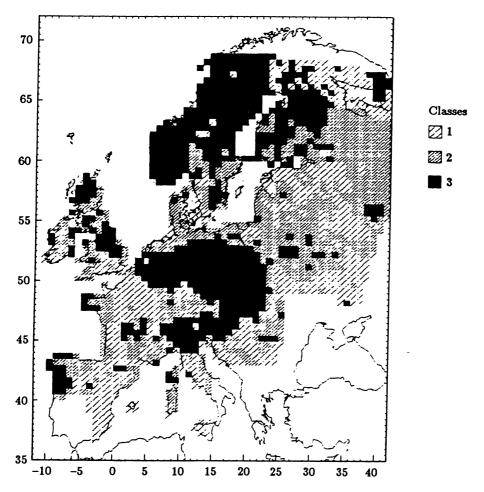


Figure 4.4. Risk of aquifer acidification. Light shading stands for low risk; dark shading represents high risk. The risk is evaluated as a combination of the sensitivity map in Figure 4.3 and the sulfur deposition pattern for the year 1980 (Alcamo et al., 1985).

recharge locations of many aquifers are unknown and may be some distance from the main body of the aquifer itself. Again, for lack of data, the neutralization potential of the soil and rocks between the root zone and the phreatic surface has not been incorporated into the methodology. As presently constructed, the methodology assumes no neutralization from this source. At present, it is not clear how to estimate the uncertainty arising from these factors.

A factor that is easier to evaluate is whether the data have been correctly divided into classes for use by the combinational algorithm. There is some judgment involved in this process with the attendant possibility of error. For any particular grid cell, changing the class assignment of one indicator may or may not cause a change in the aquifer sensitivity, depending on the values of the other indicators. For instance, if all the other indicator values are equally likely,

the probability that the sensitivity will be changed by a 1-unit error in the potential recharge indicator is only 13%. In fact, because all other indicator values are not equally likely, but are determined by the data set, the probability of changing the sensitivity is actually about 25%. This value is the maximum probability of change associated with any indicator. The probability associated with aquifer mineral composition is also 25%, followed in decreasing order by base cation content (20%), aquifer size (18%), soil depth (13%), and soil texture (9%). In contrast, the probability of changing the risk assessment by changing the deposition class of a grid cell is 69%.

The second source of uncertainty is the choice of ratings used in the matrices, reflecting the coefficients of piecewise linear functions. These are supplied by the model user, and bias may be unintentionally introduced. Test runs show that that results are relatively unaffected by reasonable changes in every functional table except the sensitivity and risk tables. The position of the table in the algorithm determines its importance to the final result (i.e., those tables closest to the sensitivity table exert greater influence on the final result than tables located earlier in the flowchart, Figure 4.2).

The third source of uncertainty is the spatial resolution of the data. The individual grid cells are larger than some essential map features, such as individual soil types and aquifers. As a result, up to seven soil types and six aquifers per grid are included in the input data set. Unfortunately, because these data were taken from different sources, they are not related spatially within the grid cell. Given these multiple readings, which soil and aquifer data should be used to represent the grid cell?

Several approaches have been tried. One is to use the dominant soil type and aquifer in each grid and ignore the rest of the data. This is the approach used in creating Figures 4.3 and 4.4. Another strategy is to combine systematically the soil types and aquifers within each grid cell, calculate the sensitivity, and choose the best or worst cases (lowest or highest sensitivity values) subject to a minimum area criterion to weed out very small, and possibly anomalous, aquifers and soils. Examples of best-case and worst-case maps are shown in Figures 4.5 and 4.6. These maps, based on the tables shown in Figure 4.2, consider only those soils and aquifers that cover at least 15% of the grid cell. The differences among the three cases can be seen if the average sensitivities and risks are compared. The average sensitivities for best, dominant, and worst cases are 1.62, 1.93, and 2.23, respectively. The average risks are 1.79, 2.13, and 2.41 for the best-, dominant-, and worst-case assessments.

A related spatial resolution problem is associated with the recharge and deposition data. Choosing a single value for each of these indicators to represent an area of 0.5 degrees latitude by 1.0 degrees longitude is a very coarse simplification, considering the variability of European climates, especially in mountainous regions.

Finally, there is the problem of method verification. To date, the results of these analyses have not been validated by comparison with field data, since such data are scarce. Point observations (Jacks et al., 1984; Soveri, 1985; and Wieting, 1986) do not contradict the assessments presented here. However, future research efforts need to focus on exploring these uncertainties and developing

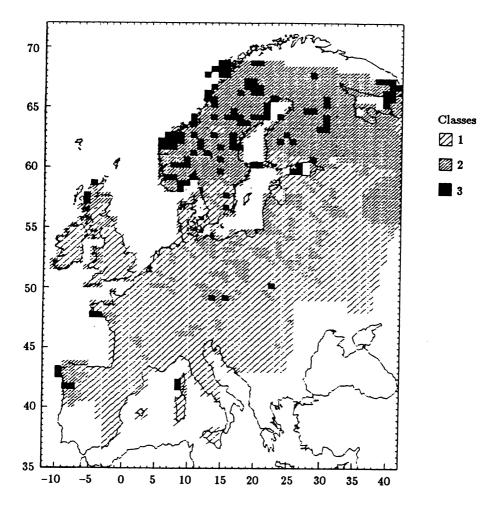


Figure 4.5. Best-case analysis of aquifer sensitivity. Within each grid cell, only those indicators are considered that combine to produce the least sensitive result.

confidence that the results of this technique are an accurate representation of reality.

4.9. Uses

This technique is not intended to predict future groundwater quality in response to continued acid inputs. The maps reflect only the sensitivities and risks of grid cells relative to each other. Nevertheless, this procedure can be used as a screening tool to locate those aquifers that are liable to experience changes first. In this way, the sensitivity and risk maps can aid in planning soil and groundwater monitoring networks. They may also guide decisions on where more detailed site investigations are warranted.

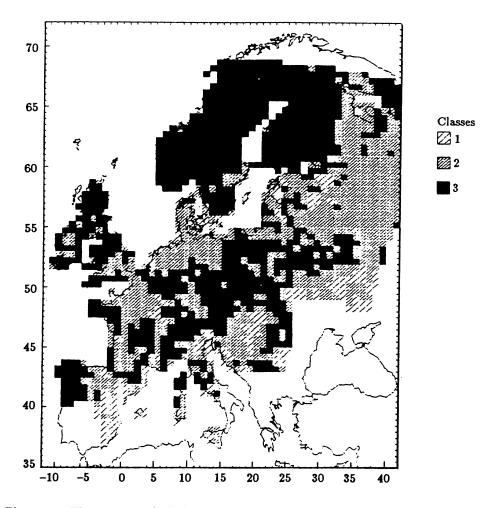


Figure 4.6. Worst-case analysis of aquifer sensitivity. Within each grid cell, only those indicators are considered that combine to produce the most sensitive result.

Although the risk assessment is ultimately based on a static database, it may be possible to use it within an overall framework of providing feedback on the future environmental effects of different air pollution control strategies. By using cumulative or time-averaged acid inputs resulting from different control strategies, maps could be produced showing the changes in aquifer risk compared with some base year.

The choice of spatial resolution strategy would depend upon the use intended for the maps. For example, planning monitoring networks may be best served by using worst-case data, while evaluating general environmental degradation in response to acid deposition might be better served by using the dominant-case calculations.

4.10. Summary

This chapter has presented an analytical technique for estimating the geochemical sensitivity of aquifers and the associated risk that groundwater quality changes may occur as a result of atmospheric acid deposition. European-scale maps prepared by this technique are also presented. Uncertainties in the resulting sensitivity and risk assessments are connected with the compilation of the sensitivity indicators, with the construction of the function matrices, and with the spatial resolution of the data. Nevertheless, the results of this technique can aid in the design of groundwater monitoring networks, and may contribute to the preparation of damage assessments associated with different air pollution control strategies.

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