Charles University in Prague
Faculty of Science

Modeling the recovery of anthropogenically acidified mountain waters

Mgr. David W. Hardekopf

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Supervisor: Doc. RNDr. Evžen Stuchlík, CSc.

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I affirm that neither this thesis, nor any of the publications attached within, has been submitted for the purpose of obtaining the title of PhD, or any other title, at another institution.

The first authors (besides me) of the papers in this thesis, namely Jakub Horecký, Jiří Kopáček, and Richard F. Wright, are aware of and agree with their inclusion here.

Mgr. David W. Hardekopf,
Institute for Environmental Studies, Charles University in Prague

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Contents

Introduction

This thesis is based on five manuscripts focused on the effects of anthropogenic acidification of ecosystems in the Czech Republic and Slovakia, and an attempt to understand the processes and time-frame of recovery using modeling. In the Tatra Mountains in Slovakia, high-mountain lakes have been the focus of long-term studies on both the biological and chemical impacts of acidification. The effects of anthropogenic acidification on headwater streams in the mountains and highlands of the Czech Republic have been recognized more recently, and the resulting changes to the biological community and course of chemical changes are less well-known. Though the modeling focuses on chemical recovery of these ecosystems, especially in the stream ecosystems, an attempt is made to evaluate the likelihood of biological recovery in the future. In addition, in two of the papers the possible influence of climate change on the recovery of these ecosystems is explored by incorporating possible scenarios into the basic acidification modeling.

The main questions that are addressed in the papers of this thesis are:

- How does the macroinvertebrate community of acidified streams reflect their chemical status
- What is the current chemical status of the Tatra Mountain lakes at this stage of their recovery?
- Can the geochemical model MAGIC be applied to the variety of high-mountain lakes in the Tatra Mountains and successfully model their different known responses to the increase and subsequent decrease in anthropogenic acidification?
- Can possible changes in climate be incorporated into the acidification model, and what does this tell us about the confounding effects of climate change on the continued recovery of acidified ecosystems?

Organization

The order of included publications has not been organized chronologically, but rather following a thematic development. The first two papers are somewhat more "basic knowledge" manuscripts providing background information for more advanced analytical papers. The first presents a summary of the macroinvertebrate communities in acidified headwater streams throughout the Czech Republic, and related pH and chemistry data. This knowledge provides a basis by which to hypothesize how the structure of these communities has been affected by low pH, and what their original composition may have been before acidification. The second paper presents the recent (2004) status of the chemistry of the Tatra Mountain lakes. In addition to quantifying the status of the chemical recovery of the lakes, this information is important in the modeling calibration process and model verification.

The next three papers deal with using the biogeochemical model MAGIC (Modeling the Acidification of Groundwater in Catchments, Cosby et al., 2001) to model surface waters in catchments affected by atmospheric acidification. The first paper outlines the application of the model to 31 lakes in the Tatra Mountains, and demonstrates the ability of the model to successfully reflect the chemical development of lakes of differing acidification responses. Also, the paper demonstrates the model's predictions for further lake chemistry recovery under current legislated emission levels. The next paper is concerned with an attempt to incorporate the effect of climate change processes into the MAGIC model. A common protocol based on a set of 8 scenarios was applied to previously-modeled freshwater ecosystems throughout Europe and North America.

The final paper in the thesis reflects an integrative approach, and includes an analysis of the macroinvertebrates of a highly acidified stream (Litavka, in the Brdy Mountains), the application of the MAGIC model to the site, and the use of a regional climate model to derive climate scenarios to predict the possible effect of an increase in temperature on future recovery. In addition, a neighboring branch of the stream with similar characteristics but different chemical status provides an approximation of a "reference" community. This allows us to estimate the original community structure of the highly affected stream, and possibilities for future recovery.

Background and Summary

1. Anthropogenic acidification of sensitive lakes and streams

Though the role of human-caused "acid rain" in the process was debated in the 1970s and early 1980s, freshwater acidification was already recognized to be a serious problem in both Europe and North America (e.g. Oden, 1968). Eventually, results from extensive surveys (e.g. Henriksen et al., 1988) and evidence from paleolimnological research (Mason, 1990) definitively implicated the role of anthropogenic emissions. Currently, anthropogenic acidification of sensitive surface waters from the deposition of sulfur and nitrogen compounds is a well-known and extensively studied phenomenon (e.g. Reuss and Johnson, 1986; Reuss et al., 1987; Driscoll et al., 1995). In Central Europe, this deposition increased markedly after the Second World War, and peaked during the 1980s, resulting in major acidification of sensitive ecosystems throughout the region (Kopáček et al., 2001, 2002). Through the toxic effects of inorganic aluminum leached at lower pH and impacts on nutrient cycling (e.g. Wetzel, 2001), acidification had a major impact on lake communities (Stuchlík et al., 1985; Sacherová et al., 2005). This was well documented in the Bohemian Forest, for instance in Čertovo Lake, where pH declined to a minimum of ~4.3 in the 1980s, and cladoceran zooplankton went extinct (Fott et al., 1994). In the Tatra Mountains, sampling programs in the 1980s (Stuchlík et al., 1985) found that zooplankton had been seriously affected in sensitive lakes above timberline. It was also recognized that these alpine lakes in this district behaved differently to comparable levels of acidifying deposition (Fott et al., 1994), and three categories were defined according to their sensitivity. This sensitivity was found to be related to prior base cation (mainly calcium and magnesium) concentrations, which in turn depend on the catchment bedrock composition, type of vegetation cover, and amounts of soils (Kopáček et al., 2006).

Though acidification was first recognized in the above-mentioned more intensively studied border mountain regions of the former Czechoslovakia (Fott et al., 1987), a study on the distribution of acidification in the Czech Republic (Veselý and Majer, 1996) showed that many streams in highland areas throughout the country were severely affected. In addition to lying on sensitive bedrock, the impact of acid deposition was compounded in many cases by the practice of planting monocultures of Norway spruce (*Picea abies*), enhancing the dry deposition of acidifying compounds (Křeček and Hořická, 2001). The highland area of the Brdy Mountains, in the central part of the Czech Republic contains many such streams, almost all heavily affected by acidification (Veselý and Majer, 1996; Horecký et al., 2002). The first paper of this thesis (Horecký et al., 2006) summarizes the chemistry and macroinvertebrates of a number such affected streams.

2. Current chemical and biological status

In response to the recognition of the anthropogenic role in acidification, international protocols were signed which were designed to reduce emissions over Europe (i.e. the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution - UN/ECE LRTAP Sulpher Protocols in 1985 and Gothenburg Protocol in 1999, UNECE, 1999). Combined with the collapse of ex-communist economies after 1989, these agreements resulted in a widespread reduction in atmospheric deposition of acidifying compounds. In Central Europe, deposition of sulfur and nitrogen decreased by about 50-80% and 30%, respectively (Kopáček et al., 2001). This substantial decline in nitrogen emissions, in particular, is unique to the region. In response to lower deposition there has been a widespread recovery from acidification in many surface waters throughout Europe and North America (Stoddard et al., 1999, Kopáček et al., 1998), though the magnitude has been variable (Evans et al., 2001). For the highland forested catchments in the Czech Republic and alpine lakes in the Tatra Mountains, the chemical response to lower deposition has also been varied (Veselý et al., 2002). In some cases, there has been a sort of hysteresis (Kopáček et al., 2002), and the levels of acidifying compounds in surface waters has not dropped as quickly as in deposition. Long-term high levels of sulfate deposition has led to its accumulation in some soils, and desorption of soil SO_4 and mineralization of sulfur from organic compounds (Novák et al., 2000) has been predicted to effect the chemistry of some catchments for decades (Hruška et al., 2002; Majer et al., 2003). The second paper in this thesis is focused on the chemical status of 91 Tatra lakes (Kopáček et al., 2006), and summarizes the state of chemical recovery 15 years after reductions in acid deposition. Atmospheric deposition of SO_4^{2-} and inorganic N decreased by 57% and 35% respectively in this region from the late 1980s to 2000. Lake water concentrations of SO_4^{2-} and NO^{3-} have decreased both by about 50% on average, but this has been variable, depending on the catchment vegetation coverage. Though pH increased most rapidly in lakes with forested catchments, acid neutralizing capacity (ANC) increased more in alpine lakes, especially in lakes with mostly rocky catchments.

The biological community response to changes in water chemistry has been varied as well. This process is not expected to always be straightforward because of the complex response of various species to changes in abiotic factors (Keller et al., 2002). In the Bohemian Forest, an experiment to reintroduce extinct zooplankton to one of the lakes was only partially successful (Kohout and Fott, 2006), even though chemical parameters had markedly improved since the peak of acidification. In the Tatra Mountains, there has been evidence of the return of some zooplankton and benthic species to some sensitive lakes, but not to others (Hořická et al., 2006; Bitušík et al., 2006), reflecting the complexity of biotic and abiotic interactions.

For sensitive streams in the Czech highlands, knowledge of the composition of biological communities before acidification is sparse (Horecký et al., 2002). In the first paper in this thesis (Horecký et al., 2006) macroinvertebrates were sampled from several sites in the Czech Republic within a narrow but low pH range (from 3.98 to 4.65) and low levels of total organic carbon, in order to assess how acidification has affected this community in these streams. Principle component analysis showed that, even in this narrow range, pH and associated heavy metals determined the number of taxa present. This work is important in both providing a comprehensive survey of the current macroinvertebrate part of the community in this type of presently acidified streams in the Czech Republic, and provides a benchmark by which future recovery can be assessed. As part of the final paper in this thesis (Hardekopf et al., 2008, see more below), the macroinvertebrates of the heavily acid Litavka River were also studied. One branch of this river in the Brdy Mountains currently has pH about 4.1, and is largely buffered by aluminium ions. However, a side branch of the uppermost reach of this river is mostly spring-fed, and is much less affected by acidification, with current pH around 5.6. This allows an analysis of the community that is likely to have been present in the more acidified branch in the past, as well as a reference by which to assess future recovery.

3. Acidification modeling

Three papers in this thesis are built around acidification modeling. One of the key concepts incorporated into acidification models has been that of a “critical load” (Posch et al., 2001), which is defined as the amount of a constant input of a particular substance that an ecosystem can tolerate over a long period of time. For acidified catchments, this generally refers to the amount of deposition of an acidifying compound, and assumes a steady-state equilibrium - so that deposition is either below or above a critical level. However, the critical loads concept does not include any information about time scales, which are important in considering the response of an ecosystem to such inputs. Therefore, “dynamic models” of acidification have been developed to incorporate the buffering mechanisms present in ecosystems, such as the cation exchange capacity, which allows an ecosystem to buffer incoming acidifying ions for some time, and delay the period before the system reaches a critical level. Dynamic models provide a mechanism for estimating the time that this process takes.

Though there are many dynamic acidification models (Tiktak & Van Grinsven, 1995), they are all based on the same principles: the charge balance of ions in the soil solution, mass balances of those ions, and equilibrium equations. One of the earliest models is MAGIC (Model of Acidification of Groundwater in Catchments, Cosby et al., 1985), which considers the stream or lake water concentrations of ions to be the result of the soil processes incorporating deposition chemistry. Later versions of the model included the dissociation of organic acids and nitrogen dynamics in the soil (Cosby et al., 1995, 2001). This model has mostly been used for smaller lake and stream catchments, and has been applied widely throughout Europe and North America. As with other models, the input data required includes deposition chemistry (including future scenarios); soil parameters (i.e. cation exchange capacity, base saturation, sulfate adsorption, exchange and equilibrium constants); weathering; and net uptake of base cations and N by vegetation.

In the Tatra Mountains, alpine lakes exhibited large differences in water chemistry trends throughout the period of increased and subsequent decrease of acid deposition, due to their catchment characteristics (Kopáček et al. 2000). In the third paper in this thesis (Kopáček et al. 2004), the MAGIC model was applied to 31 representative lakes, demonstrating the ability of the model to successfully represent this range of diversity in chemical response. In addition, predicted future emissions levels under the Gothenburg Protocol were applied to the model, and the future recovery of these lakes was evaluated. For the most sensitive lakes, even the relatively low emissions required (and already achieved) by this protocol will not allow their full recovery to pre-acidification conditions.

4. Climate change and incorporation into MAGIC

Since dynamic models such as MAGIC allow predictions of chemical conditions in the future, it is of interest to ask how predicted climate changes might affect these future states. Changes in temperature and precipitation could produce "confounding factors" (Wright and Jenkins, 2001), that influence the outcome of surface water recovery from acidification. Increases in temperature on both global and regional levels during the past century are well documented (Folland, 2001), and global climate models predict this trend will continue (IPCC 2007, http://www.ipcc.ch). Though acidification models such as MAGIC are in principle driven my levels of acid deposition to the system, many of the model parameters are directly or indirectly controlled by climate-related parameters. Precipitation and runoff, for instance, directly influence the hydrological regime and fluxes of compounds. Temperature affects many processes, such as decomposition rates, partial pressure of CO_2, growth of plants, and amounts of dissolved organic carbon, all of which eventually affect the level of acidity in surface waters. In the fourth paper in this thesis (Wright et al., 2006), the future course of several of these parameters were incorporated into the MAGIC model, and tested at calibrated sited throughout Europe and North America. This demonstrated the ability of the model to in principle predict the possible effects of climate change in these catchments. Also, the results show that some parameters had little effect on the course of soil and surface water chemistry, some were important at only a few sites, while others were important at nearly all sites.

In order to more accurately apply such possible future climate changes, it is necessary to have more detailed information about the changes that can be expected at the catchment level. General circulation models (GCM), are based on large-scale processes involving the atmospheric air masses, oceans, land surfaces, sea ice, etc. Thus, their ability to predict changes at smaller-scale regional levels is limited. However, attempts to downscale these GCMs are underway, with projects such as PRUDENCE (http://prudence.dmi.dk/) in Europe. This downscaling is accomplished through regional climate models that are applied using data from the larger GCMs to provide predictions for 50x50 km grids covering Europe from the years 2071 to 2100. Many climate-related parameters are available, such as daily averages of temperature, precipitation, evaporation, runoff, and cloudiness. This data can be used to obtain predictions specific for the region of interest.

In the final paper in this thesis (Hardekopf et al., 2008), this modeling was used at the Litavka River. The MAGIC model was calibrated to the more acidified rain-fed branch, and predictions of future trends under legislated emissions levels were predicted. Then, a regional climate model was used to estimate the increase in temperature due to climate change at the catchment. Scenarios based on empirical results from other authors were then derived that could realistically occur based on this increase in temperature, and these scenarios applied to the baseline modeling. The modeling shows an only very slow, gradual recovery of pH and alkalinity to the strongly acidified rain-fed branch of the Litavka River. While current deposition of acidifying compounds is already low, SO_4 leaching from the soil, combined with depleted soil base saturation, will continue to prevent stream pH and alkalinity from recovering to their levels before 1860. Interestingly, the influence of increased temperature in the catchment due to climate change will apparently have little impact on the prognosis for chemical recovery. This reflects the fact that despite major reductions in acid deposition, the effects of long-term exposure to acidifying emissions will continue to dominate the chemistry of some sensitive surface waters and the likelihood of their eventual biological recovery. However, other changes not incorporated into this modeling (e.g. forest decline or changes) could still have significant impacts on the future course of recovery. As in the survey of acid streams throughout the Czech Republic, the macroinvertebrate composition in the rain-fed branch of the Litavka River reflects the acidic conditions. Chronically low water pH resulted in the absence of acid sensitive taxonomic groups such as molluscs, mayflies and crustaceans, and of acid sensitive stonefly and caddisfly species. If recovery proceeds according to this modeling, some of the more acid tolerant species present in the neighboring spring-fed branch might be able to colonize the rain-fed branch, which would represent a sort of “first indicator” of biological recovery.

Conclusions

This thesis is composed of papers covering a fairly wide range of topics, from stream macroinvertebrates, mountain lake chemistry, acidification modeling, to climate change. They are all tied together, however, by the theme of acidification, what its effects have been, and what the future of affected ecosystems might be. Though acidification is considered by some to be a scientific topic whose time is largely past, our research has shown that some sensitive ecosystems are still suffering from decades of acidifying deposition. Despite years of research into "acid rain" and the acidification of fresh waters, there is still much we do not know. Legislation reducing emissions has certainly been successful in reversing acidification in many lakes and streams, but in more sensitive or heavily affected ecosystems, this is still not enough to allow their recovery to "original" conditions before the industrial revolution. Both chemical and biological recovery has been varied for different types of affected ecosystems, and modeling predicts that this situation will continue. The confounding effects of climate change will undoubtedly play some role, but our sophistication in modeling this role is still relatively low. However, it is important to show that these processes *can* be incorporated into our models, and feedback from continued monitoring will surely lead us to a better understanding of the integrated chemical and biological systems of freshwater catchments. As shown in these papers, many important steps have already been made. Knowing the past and current status of an ecosystem is extremely important in knowing how it changes in response to changing environmental conditions. Modeling results have shown that the variability of sensitive ecosystems can be successfully represented in the model framework, which increases our confidence when making prognoses of future trends. Combined with comparative studies, modeling can help fill in the gaps in knowledge about how an ecosystem has changed in the past, and show which processes are likely to be important in the future. We have also shown that the modeling can be flexible, and incorporate processes that indirectly affect recovery from acidification. And finally, modeling provides predictions that can be tested and further refined as data continue to grow.

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