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Sulphate leaching from diffuse agricultural and forest sources in a large central European catchment during 1900–2010

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HIGHLIGHTS

- Study is based on 50-year monitoring of SO_4–S export from the upper Vltava catchment.
- SO_4–S export primarily reflects hydrology and S inputs in fertilisers and deposition.
- But, mineralization and desorption contribute to SO_4–S leaching from soils.
- Leaching of accumulated SO_4–S delays recovery of surface waters from acidification.
- S losses from farmland increase a risk of S deficiency for S-demanding crops.

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ABSTRACT

Using dynamic, mass budget, and empirical models, we quantified sulphate–sulphur (SO_4–S) leaching from soils in a large central European catchment (upper Vltava river, Czech Republic) over a 110-year period (1900–2010). SO_4–S inputs to soils with synthetic fertilisers and atmospheric deposition increased in the 1950s–1980s, then rapidly decreased (~80%), and remained low since the middle 1990s. The proportion of drained agricultural land rapidly increased from 4 to 43% between the 1950s and 1990s; then the draining ability of the system slowly decreased due to its ageing. Sulphate concentrations in the Vltava exhibited similar trends as the external SO_4–S inputs, suggesting that they could be explained by changes in atmospheric and fertiliser S inputs. The available data and modelling, however, showed that (i) internal SO_4–S sources (mineralization of soil organic S in the drained agricultural land), (ii) a hysteresis in SO_4–S leaching from forest soils (a net S retention at the high S inputs and then a net release at the lowered inputs), and (iii) hydrology must be taken into account. An empirical model was then employed, based on parameters representing hydrology (discharge), external SO_4–S sources (inputs by synthetic fertilisers and atmospheric deposition), and internal SO_4–S sources (mineralization related to soil drainage). The model explained 84% of the observed variability in annual SO_4–S concentrations in the Vltava river during 1900–2010 and showed that forest soils were a net sink (105 kg ha^{-1}) while agricultural land was a net source (55 kg ha^{-1}) of SO_4–S during 1960–2010. In the late 1980s, forest soils changed from a sink to a source of S, and the present release of SO_4–S accumulated in forest soils thus delays recovery of surface waters from acidification, while S losses from agricultural soils increase the risk of future S deficiency in S-demanding crops.

1. Introduction

Since the mid-1900s, when anthropogenic acidification was recognized as a wide-spread phenomenon in many parts of Europe and North America, great progress has been made in the documentation, understanding, and modelling of sulphur (S) deposition effects on terrestrial and aquatic ecosystems (e.g. Psenner and Catalan, 1994; Norton and Veselý, 2004). Long-range atmospheric transport of S has contributed to the acidification of sensitive areas and resulted in elevated sulphate–sulphur (SO_4–S) concentrations in receiving fresh waters. In contrast to unmanaged (forest and alpine) areas, where atmospheric deposition represents the major S input, agricultural land has also received SO_4–S as a part of S-bearing synthetic fertilisers such as ammonium sulphate, potassium sulphate, superphosphate and complex fertilisers since the early 20th century (Eriksen, 2009).

Sulphur is not only an acidifying pollutant, but also an essential nutrient required for plant growth, and plays an important role in many plant processes such as synthesis of essential amino acids, chlorophyll, and fixation of nitrogen (N) by leguminous plants (Blair, 2002; Eriksen, 2009). Consequently, significant reductions in S emissions since the 1980s (Smith et al., 2011), decreasing concentrations of

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sulphate in superphosphate since the 1960s, and reduced consumption of synthetic fertilisers in many European countries since the early 1990s (FAO, 2010) have resulted in a 'surprising' phenomenon — sulphur deficiency in crops (Schnug, 1991; Zhao et al., 2002; Zelený and Zelená, 2002). Sulphur deficiency was first recognized in S-demanding crops such as canola, and since the mid-1990s also in cereals (Pedersen et al., 1998).

Large heterogeneous catchments may thus exhibit the paradoxical situation that the continuing mineralization of organic S stored in unmanaged soils may further contribute to their acidification, while S may become a limiting nutrient in some agricultural areas. Sulphate leaching from (and S accumulation in) unmanaged soils can be successfully predicted using dynamic models, e.g. MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al., 1985). The MAGIC model has been widely used in a variety of applications to simulate acidification of soils and surface waters; it simulates sulphate dynamics in terrestrial and aquatic ecosystems, based on sulphate retention/release kinetics in soils. Stable S isotope research and mass budget studies have indicated that biological S turnover is (besides adsorption–desorption) an important process in the soil S cycle (Alewell, 2001; Prechtel et al., 2003; Novák et al., 2005). Simple input–output (adsorption–desorption or immobilisation–mineralization) models provide reasonable estimates of sulphate fluxes, if they are considered as a carrier of cations from soils in acidification studies. If sulphate leaching is considered as a loss of an essential nutrient from cropland, however, additional processes affecting S cycling and pools in soils should be considered (Schoenau and Germida, 1992).

Sulphate applied to agricultural land may be (i) adsorbed in the soil, (ii) reduced and stored in vegetation, soil microbial biomass and as poorly soluble sulphides in soils and/or released to the atmosphere as H_2S, and (iii) leached (e.g., Reuss and Johnson, 1986; Novák et al., 2004, 2005; Ercoli et al., 2012). In contrast, SO_4–S may be produced in soils by mineralization of soil organic S (Ghani et al., 1993; Clark et al., 2006). Mineralization and immobilisation of S occur concurrently, and the leaching or incorporation of SO_4–S into soil organic matter is thus a net result of several processes, reflecting soil physico-chemical properties (Keer et al., 1986; Eriksen et al., 1995; Eriksen, 2009; Ercoli et al., 2012). Soil processes responsible for sulphur transformations such as oxidation and reduction are mainly microbially mediated and are therefore affected by soil permeability, aeration, moisture, pH, and substrate availability (Ghani et al., 1993; Eriksen, 1997).

The same land use changes that affect mineralization of soil organic N (e.g., drainage, tilling, water table management, conversion of arable land to meadows and vice versa; Kopáček et al., 2013a;b) may thus be important factors in the mobilisation of soil S pools in managed agricultural soils. In fact, Singh et al. (2004) reported significant reduction in soil S pools after long-term cultivation of pastures. Another important mechanism controlling sulphate retention in soils via adsorption and mineralization is soil pH. Sulphate adsorption onto Al and Fe oxyhydroxides increases as pH declines to ~3–3.5, because the total positive charge of their surface increases (Stumm, 1992). In contrast, hydroxyl anions effectively replace sulphate adsorbed in soils at higher pH (Tisdale et al., 1984). Curtin and Syers (1990) found that most of soil sulphate was in solution at $\text{pH} > 6$. Elevated soil pH after liming also temporarily increases mineralization of soil organic matter (Nyborg and Hoyt, 1978) and the increased S mineralization then contributes (besides sulphate desorption) to elevated SO_4–S leaching (Bolan et al., 1988).

Changes in land use and agricultural practices usually occur in parallel (e.g., increased fertilisation rate, soil drainage and liming), prohibiting proper disentangling of their individual effects on SO_4–S leaching. An exception to this pattern is the present development of agriculture in the Czech Republic (and other post-communist European countries) due to the abruptly decreased S inputs to agricultural land, resulting from the reduced consumption of synthetic fertilisers and a ~90% reduction in S emission/deposition rates at an otherwise stable proportion of drained soils (Kopáček et al., 2012, 2013a,b). This large-scale 'experiment' enables better understanding of the contribution of external and internal SO_4^{2-} sources (fertilisation plus atmospheric deposition versus mineralization plus desorption) to SO_4^{2-} leaching from agricultural land.

The aims of this study are (i) the quantification of S sources for forest and agricultural areas of a large heterogeneous catchment in central Europe during 1900–2010, (ii) the application of mass budget and dynamic models to estimate the role of diffuse forest and agricultural sources in the surface water pollution with sulphate, and (iii) to evaluate effects of hydrology, external S sources (atmospheric deposition and mineral fertilisers), and internal S sources (elevated mineralization after drainage and tilling of waterlogged agricultural land and reduced soil ability to adsorb sulphate after liming) on SO_4–S leaching from agricultural land.

To fulfil these aims we first estimated the major SO_4–S inputs into the catchment and measured and modelled the major export fluxes from the catchment sources to surface waters. Then we developed and calibrated an empirical model for SO_4–S leaching from agricultural land, and finally compared the export fluxes to the model estimates.

2. Materials and methods

2.1. Site description

The upper Vltava catchment (12,968 km^2, elevation 271–1378 m; Fig. 1) stretches from the mountain range between the Czech Republic, Austria, and Germany to the Slapy Reservoir, built in 1954 ~40 km upstream of Prague. The bedrock of the catchment is mostly formed by crystalline rocks, and soils are dominated by cambisols, with depths usually <1 m in steep mountain areas and >1 m elsewhere. At present, agricultural land, forests (mostly plantations of Norway spruce; *Picea abies*), surface waters, and urban areas cover 52%, 42%, 3%, and 3% of the catchment, respectively, but their proportions changed during the 20th century. The forest proportion increased from 32% to 42%, whereas agricultural land decreased from 63% to 52% between 1900 and 2010, with the major changes occurring during 1945–1947 (Kopáček et al., 2013b). The area and volume of surface waters (mostly shallow polymictic ponds) increased from ~360 to 460 km^2 and from ~0.3 to 1.66 km^3, respectively, in the study catchment between 1900 and 1991 due to the construction of eight deep valley reservoirs. Water residence times in the surface waters thus increased from 0.1–0.2 years during 1900–1960 to a wide range of 0.3–0.9 years during 1980–2010 (Kopáček et al., 2013b).

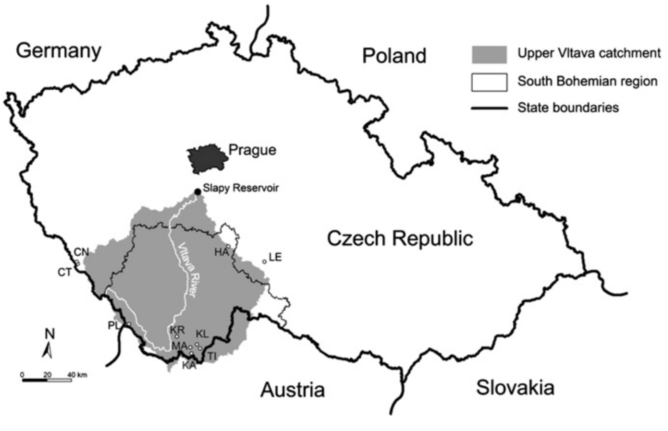

Fig. 1. Catchment of the upper Vltava river (grey area) and boundary of the administrative South Bohemian District and their location in the Czech Republic. Points with abbreviations indicate locations of the sampled forest lakes and streams (full names and other details are in Supplementary Information, Table SI-2).