Water Research 125 (2017) 374–383

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

# Trends in riverine element fluxes: A chronicle of regional socio-economic changes

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ARTICLE INFO

*Article history:*
Received 26 April 2017
Received in revised form
9 July 2017
Accepted 29 August 2017
Available online 30 August 2017

*Keywords:*
Water pollution
Hydrology
Ions
Nitrogen
Phosphorus

ABSTRACT

We show how concentrations of water solutes in the Vltava River (Czech Republic) and their riverine outputs from the catchment were modified by socio-economic changes, land use, and hydrology between 1960 and 2015. In the early 1960s, $HCO_3$ and Ca were the dominant ions. During 1960–1989 (a period of planned economy with an over-use of synthetic fertilizers, excessive draining of agricultural land and little environmental protection), the riverine concentrations of strong acid anions (SAAs: $SO_4$, $NO_3$, and Cl) increased 2–4-fold and their leaching was accompanied for by a 1.4–1.8-fold increase in concentrations of Ca, Mg, K, and Na. SAAs mostly originated from diffuse agricultural sources (synthetic fertilizers and mineralization of organic matter in freshly drained and deeply tilled agricultural land) and their annual average concentrations (as well as those of Ca, Mg, and K) were positively correlated with discharge. During 1990–2015 (a period of a re-established market economy, reduced fertilization, ceased drainage, partial conversion of arable land to pastures, and increasing environmental protection), concentrations of $SO_4$ and $NO_3$ significantly decreased due to reduced agricultural production and atmospheric pollution, and their positive correlations with discharge disappeared. In contrast, Na and Cl concentrations increased due to more intensive road de-icing, and their concentrations became negatively correlated with discharge. Trends in phosphorus concentrations reflected changes in its input by both diffuse (fertilizers) and point (wastewater) sources and were discharge independent.

## 1. Introduction

Long-term databases provide important information on ecosystem development and changes (e.g., Raymond et al., 2008; Aquilina et al., 2012; Kaushal et al., 2017). Well established water monitoring programs are necessary to identify whether an "observed change" in water composition was a part of natural year-to-year variability, a result of some accidental event, or a new beginning of a long-term response to changing socio-economic, land-use, or climatic drivers (e.g., Magnuson, 1990; Stow et al., 1998; Chapra et al., 2012). Sufficiently long time series provide a framework for tracking environmental drivers responsible for the current conditions and modelling their effects under different scenarios of their future development. Such an understanding of cause-effect responses reduces the possibility of repeating the mistakes of the past and represents a necessary background for evaluating environmental strategies and choosing the most cost-effective science-based management decisions for the future (e.g., Magnuson, 1990).

In this study, we show how time series of the Vltava (a central European river) chemistry became a valuable chronicle of socio-economic changes in its catchment during the 20th century. Regular monitoring of the Vltava chemistry started in 1959 (Procházková and Blažka, 1986, 1989). Up to now, the records enabled estimating the contribution of diffuse and point sources to water pollution with nutrients (Procházková et al., 1996; Hejzlar et al., 2016) and the disentangling of external sources (fertilizers, industry, road salts, household, and atmospheric deposition) and internal sources (mineralization of soil organic matter) of nitrogen (N), sulphur (S) and chloride (Cl) in their leaching from agricultural land (Kopáček et al., 2013a; b; 2014a; b).

The major aims of this study are (1) to show how the Vltava water chemistry has changed due to socio-economic and land-use changes in its catchment since the early 1960s, (2) to compare riverine outputs of elements with their inputs to the catchment, and (3) to show how these outputs were affected by hydrology. This

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http://dx.doi.org/10.1016/j.watres.2017.08.067

study brings new aspects to recent research on impacts of land use, management, and climate on riverine element exports from large European and American catchments (e.g., Kaushal et al., 2005, 2017; Raymond et al., 2008; Aquilina et al., 2012).

## 2. Materials and methods

### 2.1. Site description

Details on the upper Vltava catchment are given in the Supplementary Information (SI), Part SI-1. In short: The catchment (12,968 $km^2$, elevation 271–1378 m) stretches from the mountain range along the borders of the Czech Republic with Austria and Germany to the Slapy Reservoir (14.415 °E, 49.766 °N) (Fig. SI-1). The Slapy dam was built ~40 km upstream of Prague in 1954. The bedrock of the catchment is mostly formed by metamorphic rocks (gneiss, granulites, and amphibolite) and plutonic rock (granite and granodiorite). 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 area, respectively. The proportion of drained agricultural land rapidly increased from ~4% in the early 1960s to 43% in 1990; then the construction of new draining systems declined and ceased (including maintenance of the existing system) in 1994 (Kopáček et al., 2013a). Most of the drainage was done with subsurface draining systems (tubes buried 0.8–1.5 m below soil surface), with no water level control and an average lifetime of ~40 years (Kulhavý et al., 2007). The volume of surface waters in the catchment almost tripled from 0.57 to 1.66 $km^3$ in 1959–1991 due to the construction of eight reservoirs. The area of the upper Vltava catchment is almost identical to the area of the administrative South Bohemian Region (11 347 $km^2$; Fig. SI-1) with available annual statistics on agricultural activities (application of synthetic fertilizers, livestock numbers, yields of major products), industry, forestry, and population (Yearbooks by the Czech Statistical Office). We transformed these statistics from the South Bohemian Region to the whole upper Vltava catchment proportionately to their areas.

### 2.2. Socio-economical changes

The study catchment witnessed two contrary socio-economical changes typical for the Czech Republic and other European post-communist countries in the second half of the 20th century: a shift from a market to a planned economy after the Second World War and back to a market economy in the early 1990s. The major changes occurred in agriculture practices, reflecting differences between the collective and private ownership of land, and in air pollution (Kusková et al., 2008; Kopáček et al., 2013a; b; 2016). The proportion of agricultural land in huge cooperative and/or state farms increased to >80% due to the "collectivization" of agriculture (Bičík et al., 2001). Prices of agricultural inputs and products were planned, state guaranteed, and largely independent of the international market, which led to ineffectively high use of synthetic fertilizers and often excessive drainage of agricultural land (Kopáček et al., 2013a; b). The rate of consumption of synthetic fertilizers and lime rapidly grew during this period (Fig. SI-2). In addition, the post-war shift from a light to heavy industry required a rapidly increasing energy production that was mostly based on coal and lignite burning, which led to high emissions of S and N oxides and industrial dust (Kopáček et al., 2016). Increasing wood pulp and paper production in the study catchment contributed to water pollution with S compounds (Kopáček et al., 2014a), and increasing use of household detergents became an important phosphorus (P) source (Hejzlar et al., 2016).

The shift from a planned back to a market economy resulted in a temporary recession and massive restructuring of the economy in the early 1990s (Ščasný et al., 2003; Kusková et al., 2008). Benefits of farms rapidly decreased due to dramatically increasing prices of agricultural inputs (e.g., fertilizers), approaching those on the international market, without a proportional increase in prices of agricultural products. This disproportion was caused by the absence of agricultural subsidies. Some agricultural land (especially grassland) was abandoned, arable land at high elevations was changed to pastures, and agricultural production in general was de-intensified, and decreased (Bičík et al., 2001; Kusková et al., 2008). Political and economic changes after 1990 also resulted in rapid decreases in S and N emissions due to reduced coal combustion and energy and livestock production, and the installation of S and N emission controls (Kopáček et al., 2016). A continuous collapse of some industrial activities (e.g., wood pulp production) and legislative restrictions (e.g., use of phosphate in detergents) caused a decreasing use of S and P (Kopáček et al., 2014a; Hejzlar et al., 2016; respectively).

### 2.3. External element inputs to the catchment

External input of S, Cl, N, P, K, Na, Ca, and Mg to the catchment was estimated as the sum of their inputs by synthetic fertilizers, lime, atmospheric deposition, road de-icing and other sources (industrial, agricultural and household) as follows:

(1) The element inputs by fertilizers and lime only included their synthetic and mineral compounds, because organic fertilizers usually originate from plant and animal production within the large catchment and are thus part of the internal element cycling. For details on elemental contents and application rates of individual fertilizers and their historical developments during the study period see Part SI-2.

(2) Atmospheric deposition of elements was calculated as bulk deposition to the treeless area and total (bulk plus dry) deposition to forested areas. Total deposition to forests was calculated from bulk deposition using dry deposition factors ($f$). The $f$-values for ammonium, nitrate, and sulphate were estimated by Kopáček et al. (2012; 2013a; 2014a) and are time-dependent. For other elements, we used a constant $f$-value of 1.88 for the whole study period. This constant was based on throughfall and bulk deposition of conservative ions (Cl, Na, $SO_4$ and $NO_3$), which were negligibly affected by canopy leaching in the study catchment. Atmospheric deposition of N was the sum of $NH_4$–N, $NO_3$–N and total organic N (TON) (Fig. SI-3b). The trends in atmospheric deposition of ions were based on measured data from the early 1980s to 2015. Earlier data were modelled from emission rates of $SO_2$, $NO_x$, $NH_3$, and industrial dust, using relationships between the measured deposition of ions and the respective individual emission rates (Kopáček et al., 2012, 2016). Depositions of TON and total P were based on measured data at the Slapy Reservoir from 1979 and 1986, respectively, to 2016. We are aware that atmospherically deposited $NH_4$–N, TON, P and base cations (BCs = sum of K, Na, Ca, and Mg) originated to some extent from local sources, like dust emitted from fields, pollen, and $NH_3$ emissions from livestock production. The $NH_3$ emissions in the Czech Republic were, however, lower than in surrounding countries, and dust from energy production and industrial sources represented the dominant source for atmospheric BCs in the Czech Republic during the whole study (Kopáček et al., 2012, 2016). Consequently, we did not subtract the internal emission sources of N, P and BCs from their atmospheric deposition. Hence, the atmospheric fluxes of these elements used