Science of the Total Environment 518–519 (2015) 117–129

Contents lists available at ScienceDirect

Science of the Total Environment

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

Impact of reduced anthropogenic emissions and century flood on the phosphorus stock, concentrations and loads in the Upper Danube

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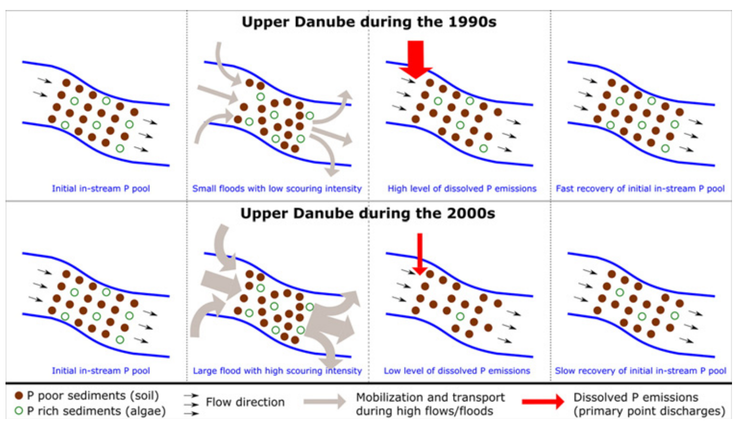
HIGHLIGHTS

- Decline of baseflow P concentration in the 1990s due to point discharge reduction.
- Despite reduced emissions, high loads in the 1990s due to pool of P rich sediments.
- Sharp and enduring decline of TP concentration at all flow levels after 2002 flood.
- Depletion of P rich sediments and long-lasting low riverine loads after 2002 flood.
- Effects of point discharge reduction visible only after depletion of P rich pool.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2014
Received in revised form 24 February 2015
Accepted 24 February 2015
Available online 6 March 2015

Editor: D. Barcelo

Keywords:
Danube
Phosphorus
Flood
Stock
Mobilization

ABSTRACT

Patterns of changes in the concentration of total and soluble reactive phosphorus (TP, SRP) and suspended sediments at different flow levels from 1991 to 2013 in the Austrian Danube are statistically analyzed and related to point and diffuse emissions, as well as to extreme hydrological events. Annual loads are calculated with three methods and their development in time is examined taking into consideration total emissions and hydrological conditions. The reduction of point discharges achieved during the 1990s was well translated into decreasing TP and SRP baseflow concentrations during the same period, but it did not induce any change in the concentrations at higher flow levels nor in the annual transport of TP loads. A sharp and long-lasting decline in TP concentration, affecting all flow levels, took place after a major flood in 2002. It was still visible during another major flood in 2013, which recorded lower TP concentrations than its predecessor. Such decline could not be linked to changes in point or diffuse emissions. This suggests that, as a result of the flood, the river system experienced a significant depletion of its in-stream phosphorus stock and a reduced mobilization of TP rich sediments afterwards. This hypothesis is corroborated by the decoupling of peak phosphorus loads from peak maximum discharges after 2002. These results are highly relevant for the design of monitoring schemes and for the correct interpretation of water quality data in terms of assessing the performance of environmental management measures.

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.087

1. Introduction

The Danube is the second largest river in Europe and is responsible for almost 60% of the freshwater and for the majority of sediments and nutrients entering the Black Sea (Maksimovic and Makropoulos, 2002; Schreiber et al., 2005). Consequently its elevated transport of phosphorus was identified as one of the main causes of the severe eutrophication that affected the sea during the 1980s and early 1990s (Kroiss et al., 2006). The control of phosphorus pollution in the Danube is therefore of primary importance, both to sustain the ecological health of the river itself, and to reduce the loads transported downstream.

Austria accounts for 10% of the total area of the Danube Basin, which drains more than 96% of its territory (ICPDR, 2014a). In the last 30 years the country has undertaken several efforts to reduce phosphorus emissions. In the 1980s the use of phosphates in detergents was dramatically reduced (Behrendt et al., 2005) and in the 1990s the Austrian edict BGBl. Nr. 180/1991, later replaced by the BGBl. Nr. 210/1996, introduced the mandatory removal of phosphorus in wastewater treatment plants (WWTP). Moreover, the agri-environmental program PUL was launched in the year 2000 to address diffuse nutrient losses (BMLFUW, 2000). In addition to anthropogenic changes, the Upper Danube Basin was also exposed to extreme hydrological conditions. After a succession of flood-poor decades, with the exception of a minor event in 1991, the Austrian Danube was hit first in August 2002 by a flood that, due to its extension and duration, was termed a "century flood", and then in June 2013 by one of the largest floods to have taken place in the last two centuries (Blöschl et al., 2013). In 2003, on the contrary, the whole Basin experienced a pronounced drought, with below-average rainfalls and above-average temperatures. The relative precipitation recorded in Austria in that year, for example, corresponded to 74% of the long-term annual average (ICPDR, 2014c).

At the beginning of the 1990s an extensive monitoring network was set up by two independent agencies, the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management (BMLFUW) and the International Commission for the Protection of the Danube River (ICPDR). It is thus feasible to examine in detail this period of combined anthropogenic changes and extreme hydrological regimes, which represent an exceptional opportunity for exploring interweaving causalities in a large river.

The link between improved wastewater phosphorus removal and decline in phosphorus concentration in European rivers has been demonstrated and quantified in previous studies (Neal et al., 2010; Räike et al., 2003). Conversely, investigations dealing with episodic flood events, total emissions, and their relationship have focused on riverine loads (mass time^{-1}), rather than on concentrations (mass volume^{-1}). Behrendt and Opitz (2000) observed, across 100 basins in Europe, a considerable discrepancy between total emissions and measured transport loads, with the latter being significantly lower. They found that the difference increased as a function of the specific runoff of the basins. Similar findings were reported by Zessner and Kroiss (1999) for the Upper Danube. The reason for such discrepancies lies in the retention process, which has been increasingly recognized as a relevant mechanism to be further investigated and included in river basin models (de Klein and Koelmans, 2011; Venohr et al., 2011). The retention of phosphorus takes place essentially through deposition and algae growth. The stock generated is then exposed to remobilization during flood events, when peaks of phosphorus are transported downstream and exported to river banks and flooded areas (Zessner et al., 2005; House et al., 1997; Dorioz and Ferhi, 1994; Johnson et al., 1976). According to Stamm et al. (2014), this depletion is replaced by the deposition of particulate phosphorus during the recessional part of the storms, which represents a renewed internal source of baseflow phosphorus. Although this might hold true for small episodic events, the impact of a major flood could be more intense and exert a more profound impact on both the in-stream stock and the concentration, with consequences not only for the peak transport of phosphorus to downstream standing water bodies and to the lateral river system, but also for the river ecology itself.

In this study, time series of water quality data of the Upper Danube are examined to identify patterns of change in phosphorus concentration, and to link them to anthropogenically driven changes and to extreme hydrological conditions. The aim of the work is to assess the performance and effectiveness of environmental management strategies, and to investigate the short-term and long-term impact of large episodic events on the in-stream phosphorus concentration and on the stock of the river system.

To gain a deeper insight into the drivers of shifts in concentration, not only is total phosphorus (TP) analyzed, but also soluble reactive phosphorus (SRP, equivalent to orthophosphate) and suspended sediments (SS). SRP contributes to identifying the impact of point emissions, because it is typically the prevalent phosphorus species in WWTP effluents (Jarvie et al., 2006). SS provides further information regarding diffuse pathways, because particulate-bound phosphorus is the predominant species transported by storm-dependent agricultural runoff and erosion processes (Withers and Jarvie, 2008).

2. Materials and methods

2.1. Data sets

The Danube was analyzed at its entrance into Austrian territory from Germany (Inflow) and at its exit from Austria (Outflow) (Fig. 1). This enables the phosphorus contribution within the Austrian catchment to be determined.

The study used a collection of different data sources, namely the H_2O database created and maintained since 1991 by BMLFUW (2014b), and two ICPDR databases, one obtained through a first campaign performed from 1992 to 1998 (Bucharest Declaration data set) and the other through the Transnational Monitoring Network (TNMN) launched in 1996 (ICPDR, 2014b). In addition, for the Outflow a specific sample collected during the flood of August 2002 (Zessner et al., 2005) and a data set of semi-continuous measurements for the entire year 2013 (BMLFUW, 2013) were available (Tables 1 and 2). Since 1991 the monitoring of surface and groundwater water quality in Austria has been regulated by federal legislation (BGBL Nr. 338/1991 replaced by BGBl. II Nr. 479/2006) that specifies the standard analytical procedures to be followed for each parameter. With respect to total phosphorus and phosphorus compounds, at the beginning of the 1990s analyses were required to comply with the Standard Ö-NORM M 6237:1986, which was then replaced by ISO 6878:1998 and later revised by ISO 6878:2004. These standards all maintained the spectrometric determination using ammonium molybdate as basis. Although accredited laboratories are entitled to apply different methods, they are required to prove their equivalence to the standard procedures. These protocols were applied by all data sources considered here. This ensures a substantial consistency of the analytical methods throughout the studied time period, although some minor variations cannot be entirely excluded. In addition, the analyses of each sample have been run in triplicate in accordance with the aforementioned protocols, with the exception of the data set of Zessner et al. (2005), which relies on single tests.

2.2. Data set subdivision in time periods and flow intervals

Phosphorus concentration and species fractionation can vary largely as a function of flow levels due to differing primary pathways and driving natural processes. TP concentration generally rises at increasing flow levels due to the higher transport of particulate-bound phosphorus in more turbulent conditions (Zessner and Kroiss, 1999). On the contrary, SRP concentration is expected to be higher at baseflow conditions, because its primary pathway is the quasi-constant WWTP effluent discharge, which becomes more heavily diluted at higher flows (Jarvie