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Catchment controls on solute export

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ABSTRACT

Dynamics of solute export from catchments can be classified in terms of chemostatic and chemodynamic export regimes by an analysis of concentration–discharge relationships. Previous studies hypothesized that distinct export regimes emerge from the presence of solute mass stores within the catchment and their connectivity to the stream. However, so far a direct link of solute export to identifiable catchment characteristics is missing. Here we investigate long-term time series of stream water quality and quantity of nine neighboring catchments in Central Germany ranging from relatively pristine mountain catchments to agriculturally dominated lowland catchments, spanning large gradients in land use, geology, and climatic conditions. Given the strong collinearity of catchment characteristics we used partial least square regression analysis to quantify the predictive power of these characteristics for median concentrations and the metrics of export regime. We can show that median concentrations and metrics of the export regimes of major ions and nutrients can indeed be inferred from catchment characteristics. Strongest predictors for median concentrations were the share of arable land, discharge per area, runoff coefficient and available water capacity in the root zone of the catchments. The available water capacity in the root zone, the share of arable land being artificially drained and the topographic gradient were found to be the most relevant predictors for the metrics of export regime. These catchment characteristics can represent the size of solute mass store such as the fraction of arable land being a measure for the store of nitrate. On the other hand, catchment characteristics can be a measure for the connectivity of these solute stores to the stream such as the fraction of tile drained land in the catchments. This study demonstrates the potential of data-driven, top down analyses using simple metrics to classify and better understand dominant controls of solute export from catchments.

1. Introduction

The temporal and spatial variability of solute export from catchments affects water quality and ecosystem health in the downstream receiving water bodies. Solute export variability is a result of natural processes like chemical weathering, climatic conditions as well as human impacts by agricultural land use and wastewater discharge. For instance nutrient fluxes from catchments intensively managed for agriculture are known to be orders of magnitudes higher than from pristine watersheds (e.g. [1]). Moreover, nutrient concentrations can have a distinct temporal variability [2,3]. Elevated nitrogen and phosphorus fluxes and their temporal variability are linked to eutrophication processes in downstream lakes, reservoirs and marine water bodies (e.g. North Sea, [4]). River ecosystem community structure and metabolic activity are known to directly responses to the temporal variability of discharge, turbidity and nutrient availability [5–7]. There is a need to understand, quantify and generalize solute export to enable better predictions of how catchment functions, such as nutrient mobilization and retention, may respond to changing conditions (e.g. climate and land use changes). However, the structural complexity of catchments and the range of interacting hydrological and biogeochemical processes at different spatial and temporal scales challenge this objective. As a general way forward to meet this challenge we propose a top down analysis of the integral, larger-scale response of the catchment to identify and separate dominant processes and controls of solute export ("pattern to process", [8]). Findings from such an analysis should in turn be used for bottom up studies to refine knowledge on systems functioning e.g. by measurements and experiments on the smaller scale of processes.

A data-driven top-down evaluation of catchment-scale solute export includes a joint assessment of concentration and discharge variability (e.g. [9]). There are numerous studies proposing top down methods to describe and understand this variability at smaller time scales from single storm events [10,11] to seasonal behavior [12–14]. However, for a robust evaluation of long term discharge and concentration probabilities a maximum range of catchment responses and thus preferably long and temporally highly resolved time series of

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concentration and discharge are needed. Such data are highly sought after but only rarely available to date [15]. However, various monitoring programs, e.g. operated by environmental authorities within the context of the EU Water Framework Directive, provide long term temporally less resolved time series containing rich information on solute and discharge probability [16,17]. A series of recent studies more systematically explored the concentration/load–discharge relationships by using such long term time series from a broad range of catchments looking for commonalities in solute export behavior [18–21]. These studies define chemostatic (concentration does not change with changing discharge) and non-chemostatic (chemodynamic) behavior of catchments by means of different metrics. These metrics are based on the concentration–discharge relationship [20], load–discharge relationship [18,22], temporal inequality of discharge and load [9,23] or the coefficient of variation of discharge and concentration [21]. The proposed metrics of solute export behavior are not only valuable tools to characterize and compare different solutes and catchments, but also provide deeper insights into the filtering functionality of catchments converting time series of external drivers (e.g. precipitation) to a discharge and concentration/load response [23].

Most previous studies have explored possible reasons for an observed chemostatic and non-chemostatic export behavior. A chemostatic export regime was found for a range of catchments for weathering products such as Na, Mg, Ca and Si [20] and on the inter-annual scale for nitrate and total P [18, 21]. These studies have related the observed chemostatic behavior either to the large, practically unlimited solute store in catchments with a long history of agricultural use or to a constantly high production and mobilization. Thompson et al. [21] showed that a chemostatic response in nitrate becomes more pronounced with increasing export loads. The authors argue that intensive management in these agricultural catchments has led to large nitrate stores in the catchment resulting in a transport limited and more predictable nitrate export. In the same way catchments with high inputs of solutes such as Na, Cl, and SO_4 from exogenous sources (via atmospheric deposition) can lead to a build-up of legacy stores and hence similarly to chemostatic behavior of these substances [21]. On the other hand, a chemodynamic export regime can result from a time variant connectivity between zones where solutes are stored and discharge generating zones within the catchment [18]. This is often the case for dissolved organic carbon, which is mobilized from upper soil horizons, which represent a carbon store and promote fast runoff during high flow periods [24,25]. Chemodynamic export behavior has also been described for suspended solids and substances strongly sorbed to solid particles (e.g. phosphorous) as a result of an intermittent threshold driven mobilization as well as for highly reactive solutes (e.g. ammonia), which are susceptible to transformation under fluctuating physicochemical boundary conditions [21]. Overall these studies hypothesize that catchment solute exports typically exhibit consistent patterns as a result of solute availability and spatial distribution in the catchment, the hydrologic connectivity of the solutes stores to the receiving surface water as well as processes within the surface water.

To date, metrics characterizing solute export have been used with a focus on similarities in the export behavior of nutrients and geogenic solutes across a range of catchments. However, there is a lack of studies exploring distinct differences in the solute export behavior of catchments, i.e. the linkage between the export behavior and the main factors influencing solute availability and mobilization such as land use and geology. Such linkages have been investigated for the mean or median of concentration time series. For instance, positive correlations between mean annual N- and P-species concentrations and the fraction of agricultural land have been described by [26, 27]. Kamjunke et al. [12] and Kyllmar et al. [28] found similar correlations on the basis of singular sampling campaigns. Onderka et al. [29] and Sliva et al. [30] showed that the geological settings and soil types were significantly related to mean annual chemical loads of nutrients to the surface waters. Statistically significant correlations between such metrics and catchment characteristics can hint at dominant controls of mean solute concentrations in catchment outflow and can often be related to agricultural management and other anthropogenic impacts on the catchments. In turn mean concentrations may be inferable from catchment characteristics as statistical predictors. We want to expand on this general idea and explore the utility of such statistic metrics to define and characterize solute export regimes of catchments.

1.1. Hypothesis

In this study, we analyzed concentration–discharge relationships for 16-year time series of surface water quality and quantity from seven sub-catchments within the 3300 km^2 central-German Bode River catchment as well as two neighboring catchments (not draining into the Bode River). The investigated catchments span strong gradients in land use, geology and climatic conditions. We hypothesize that these gradients in catchment characteristics have strong explanatory power for both, median solute concentrations as well as the export regime (e.g. chemostatic vs. chemodynamic) of different solutes. To this end, we quantify the strength of the link between catchment characteristics and median solute concentrations and metrics defining the export regime, respectively, using partial least squares regression analysis. Based on this analysis we discuss the potential causes for either chemostatic or chemodynamic export behavior as defined by [18,20,21,24]. Finally we synthesize major controls of median concentrations and export regime in a unifying scheme of the presence of solute mass stores in catchments and their connectivity to the stream as well as processes within the stream.

2. Materials and methods

2.1. Study site

The nine studied catchments consist of seven sub-catchments within the Bode River catchment in central Germany as well as two neighboring catchments of similar size (Fig. 1) draining elsewhere. The Bode River catchment is one of the observatories of the TERENO initiative [31]. TERENO (Terrestrial Environmental Observatories) aims at a long-term integrated monitoring of catchments across Germany to assess the impact of climate and land use change on terrestrial ecosystems. The Bode River catchment stretches from the Harz Mountains to the Central German Lowlands and covers an area of 3200 km^2.

The upland catchments HOL, BOD, RAP, HAS, SEL and WIP (within the Harz mountains) and the lowland catchments GGR, GEE and ALL (within the Central German lowland) define strong gradients in land use as well as the climatic, hydrologic and geologic settings (Tab. 1). Mean annual precipitation was derived from a 4 km grid of precipitation data between 1960 and 1990 [32]. Mean precipitation is considerable higher in the upland catchments (area weighted mean 879 mm a^{-1}) than in the lowland catchments (568 mm a^{-1}). This also holds true for discharge (474 mm a^{-1} in uplands, 70 mm a^{-1} in lowlands) and runoff ratio (area weighted mean 0.52 in uplands, 0.12 in lowlands). The base flow index BFI was determined on the basis of mean daily discharge measurements between 1993 and 2004 using the local minimum method in the WHAT-tool [33]. BFI is higher in the lowland catchments (area weighted mean of 0.86) than in the upland catchments (0.73). This agrees with the geological settings [34]: The upland catchments are characterized by metamorphic greywacke, slates and distributed carbonates (79.6% of total area) and by igneous rocks (20.2%) with an overall low capacity to store and transmit groundwater. The lowland catchments are dominated by Quaternary and Holocene clastic sediments, tills and loess (55.0%) and Mesozoic sedimentary rocks (40.2%) providing deeper porous aquifer systems.