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Reconciling monitoring and modeling: An appraisal of river monitoring networks based on a spatial autocorrelation approach - emerging pollutants in the Danube River as a case study

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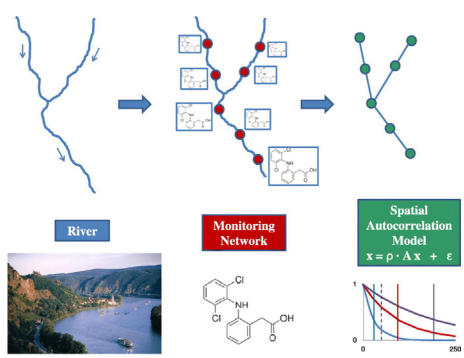
HIGHLIGHTS

- Our river perception is based on monitoring network measurements.
- Autocorrelation models for 235 emerging pollutants in the Danube River are set.
- Correlation lengths are derived from the spatial variation of autocorrelation indexes.
- 27% compounds out of 235 have a sub-optimal monitoring network.
- Neighbors vs. local relative contributions of monitored variables are quantified.
- For 92% compounds local contributions dominate over neighbors influence.

GRAPHICAL ABSTRACT



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ABSTRACT

Rivers extend in space and time under the influence of their catchment area. Our perception largely relies on discrete spatial and temporal observations carried out at certain sites located throughout the catchment (monitoring networks, MN). However, MNs are constrained by (a) the distribution of sampling sites, (b) the dynamics of the variable considered and (c) the river hydrological conditions. In this study, all three aspects were captured and quantified by applying a spatial autocorrelation modeling approach. We exemplarily studied its application to 235 emerging contaminants (pesticides, pharmaceuticals, and personal care products [PPCP], industrial and miscellaneous) measured at 55 sampling sites in the Danube River. 22 out of the 235 compounds monitored were present at all sites and 125 were found in at least 50%.We first calculated the Moran Index (MI) to characterize the spatial autocorrelation of the compound set. 59 compounds showed MI ≤ 0, which can be interpreted as 'no spatial correlation'. Next, spatial autocorrelation models were set for each compound. From the autocorrelation parameter ρ, catchment average correlation lengths were derived for each compound. MN optimality was examined and compounds were classified into three groups: (a) those with $\rho \leq 0$ [25%]; (b) those with $\rho > 0$ and correl. length < average distance between consecutive sites [2%] and (c) those with $\rho > 0$ and correl. length > average distance between consecutive sites [73%]. The MN was considered optimal only for the latter class. Networks with the larger average distance between consecutive sites resulted in a decreasing number of optimally monitored compounds. Furthermore, neighbors *vs.* local relative contributions were quantified based on the spatial autocorrelation model for all the measured compounds. The results of this study show how

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autocorrelation models can aid water managers to improve the design of river MNs, which are a key aspect of the Water Framework Directive.

1. Introduction

Rivers act as net receivers of anthropogenic pollutants (Sabater et al., 2016) such as nutrients, metals as well as a plethora of organic micropollutants (Meybeck, 2004; Schwarzenbach et al., 2006; Schwarzenbach et al., 2010). Chemical pollution has been considered one of the main drivers of freshwater biodiversity (Malaj et al., 2014). Many chemical pollutants are not environmentally persistent; rather they undergo changes due to multiple biotic and abiotic processes taking place in rivers, giving rise to additional transformation products and to complex chemical and break-down product mixtures. Rivers extend more or less continuously in space and time under the influence of their catchment area. Since only a few variables can be measured with the highest resolution in time (on-line sensors) or in space (remote sensing), and none in both dimensions, our understanding of the river qualitative status relies on discrete spatial and temporal observations of a set of physical, chemical or biological parameters, organized under what it is commonly known as a "monitoring network" (Fig. 1). Owing to the relevance of water for human consumption and the need for preserving the ecological status of freshwater ecosystems, during the last decades, a huge effort has been dedicated, either at national and supra-national scales, to gather data to fill in river monitoring network databases. The most extensive databases include those carried out by water authorities for the chemical and ecological status assessment and management of the water resources under the Water Framework Directive in Europe (Directive 2000/60/EC, 2000), and those obtained by researchers principally to evaluate the occurrence and environmental influence of multiple stressors as part of large national and international projects e.g. NORMAN ((www.norman-network.net; www.normandata.eu/empodat/)), SOLUTIONS (Altenburger et al., 2015), GLOBAQUA (Navarro-Ortega et al., 2015), DANCERS (Chapman et al., 2016), SCARCE (Navarro-Ortega et al., 2012). Data exploitation from available databases is typically carried out making use of a variety of univariate and multivariate statistical techniques, commonly employed on environmental chemometrics (Einax et al., 1997; Massart, 1998; Dietze et al., 2001; Hanrahan, 2008; Peré-Trepat et al., 2007; Terrado et al., 2009; García-Reiriz et al., 2014; Kovács et al., 2014; Rico et al., 2016). To cope with the obvious inherent limitations of experimental data obtained from discrete monitoring networks, dynamic modeling of chemical's fate and transport processes raised as a complementary alternative (Johnson et al., 2008). Modeling efforts have been mostly focused on the prediction of environmental concentrations of pollutants and to a lesser extent to their emissions as well. Existing models for concentration prediction include GREAT-ER (Feijtel et al., 1997), PhATE (Anderson et al., 2004), LF2000-WQX (Keller and Young, 2004; Johnson et al., 2007), STREAM-EU (Lindim et al., 2016; Osorio et al., 2012). Regarding emission of chemicals, estimations are based on the market volume (kg of chemical sold/year), basin population (Pistocchi and Loos, 2009; Pistocchi et al., 2012), inverse modeling (Banjac et al., 2015; Boxall et al., 2014) and WWTP removal rates (Verlicchi et al., 2012; Verlicchi et al., 2014). While modeling is undoubtedly a cost-efficient tool compared to large monitoring campaigns, its validation requires contrasting measurement data. Furthermore, parameterization needed by models (i.e., attenuation

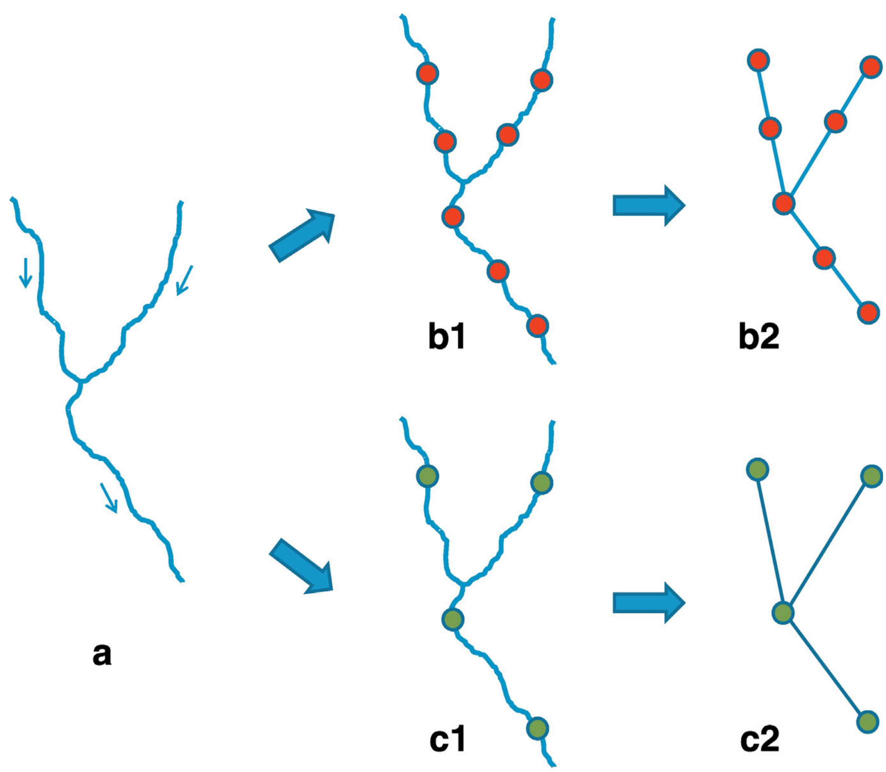

Fig. 1. **(a)** The real river stretch; **(b1, c1)** two monitoring networks of different "resolution" deployed in the same river stretch; **(b2, c2)** the corresponding graph networks associated with the monitoring networks.