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Catchment scale modelling of micro and emerging pollutants

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Catchment scale modelling of micro and emerging pollutants

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First, think. Second, believe. Third, dream.
And finally, dare.

WALT DISNEY

Abstract

The fate and transport of solutes introduced into a watershed and sampled at the catchment outlet depends on many environmental, chemical and hydro-climatological forces. Moreover, if the solutes are micro and emerging pollutants (i.e. pharmaceuticals), which are non-regulated contaminants not routinely monitored but often-detected in fresh waters, the description of the transport sources and routes becomes an interesting and challenging topic to investigate and describe, especially in conjunction with the well-known travel time transport approach at the catchment-scale. In fact, with the travel time approach to pharmaceuticals represents a framework that allows dealing in a unitary and simple way the main two mitigation mechanisms controlling them, which are dilution and biological decay. Moreover, possible consequences on the health of humans and of aquatic organisms have become issue of increasing concern by the scientific community worldwide. The topics have been extensively studied in the last decades, with some recent benchmark contributions. Nevertheless, there is still room for further development for emerging contaminant models and there is still the necessity of complementing the applications with measured data. This doctoral thesis aimed at contributing with new insights into the multi-faceted aspects of solute transport at catchment-scale, proposing novel solutions, with applications to real-world case studies and including a detailed description of the major aspects that influence the water quality dynamics in rivers. The thesis is divided into three interconnected and chronological subsequent parts. In the first part, a detailed description of three large European river basins are presented (i.e. Adige, Ebro and Sava), believing that an

accurate analysis of existing information is therefore useful and necessary to identify stressors that may act in synergy and to design new field campaigns. In addition, a detailed data analysis of the main water quality variables is presented: advanced statistical analyses (i.e. Spearman rank correlation, Principal Component Analysis, and Mann-Kendall trend tests) were applied to long-term time series of water quality data both in the Adige River Basin and in the Ebro and Sava catchments, aiming at providing an integrated and comparative analysis of recent trends, in order to investigate the relationships between water quality parameters and the main factors controlling them (i.e. climate change, streamflow, land use, population) in the Mediterranean region. These catchments are included into the EU project "Globaqua ", dealing with the analysis of the combined effect of several stressors on the freshwater ecosystems in Mediterranean rivers. In fact, little attention has been paid to linkages between long-term trends in climate, streamflow and water quality in European basins; nevertheless, such analysis can represent, complementary to a deep knowledge of the investigated systems, a reliable tool for decision makers in river basin planning by providing a reliable estimate of the impacts on the aquatic ecosystem of the studied basins. In the second part, sampling campaigns performed in our study basin, the Adige catchment, are presented in detail. Special attention is also given to emerging pollutants, whose study on the occurrence patterns and spatiotemporal variability in the Adige River Basin has been conducted in conjunction with population patterns and touristic fluxes. In the third and last part, novel theoretical solutions of the well-known advection-dispersion-reaction (ADR) equation are presented. The theory was developed for both general water quality variables and pharmaceuticals, evidencing differences and analysing the main factors that influence water quality dynamics. An application is also proposed to the Adige catchment.

DEDICATION AND ACKNOWLEDGEMENTS

When I started this PhD, I was not completely consious of the multitude difficulties that I would have encountered on the path. Nevertheless, I did not realise how the PhD could represent a training process both as a researcher and as a woman; only now I can assert that surely it has been a truly life-changing experience for me and it would not have been possible to achieve without the support of many people.
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CHAPTER 1

INTRODUCTION

The anthropogenic pressure on water resources is growing worldwide, and reducing its effects on the ecosystem is one of the major challenges to target in the near future [20, 100, 115, 136, 188]. Acquaintance of the complex ties between hydrological, geochemical and ecological stressors in large river basins (e.g., 10,000 km^2 or more) is still erratic and further researches are needed to support decisions about water resources management at the catchment scale [12, 36, 158, 191]. Even more complex but appropriate operational strategies may be prioritized,considering economical and societal constraints [25, 183].

Furthermore, additional attempts are required to better understand and quantify the contaminants' fate at the river basin scale [26, 72, 153]. Simultaneously, the analysis, within a coherent framework, of the impact of micro and emerging pollutants [126], diffused sources of pollution (e.g. [154]) on freshwater ecosystems, is a challenging task. Modeling the impact of hydrological (e.g. [1]) and chemical stressors (e.g. [90])

on freshwater ecosystems is also an open issue for large catchments. In particular, the inclusion of feedback mechanisms, which associate ecosystem functioning and anthropogenic activities to water resources management and chemical fluxes [81], represents a challenge. In order to examine these three topics, i.e., changes in the hydrological traits of large catchments, the fate and transport of pollutants in the environment and the interaction with the ecosystem (including human activities), it is crucial to have access to all available information. In particular, it is necessary, for gaining a global perspective, to integrate data collected by water authorities and environmental protection agencies operating in the river basin, whose results are published in both peer reviewed journals as well as in technical reports and other types of gray-literature (e.g.[182]). Nevertheless, a data integration of other chemicals not routinely monitored but detected in surficial waters must be planned and perfomed.

The present thesis is structured as follows:

- Chapter 2 presents a description of the study basins (2.1), of the available data (2.2), including the information gathered through ad-hoc sampling campaigns, and introduces the statistical methods adopted for the analyses and the mathematical framework of a novel transport model (2.3);

- Chapter 3 shows the main outcomes of the driver detection of water quality trends in three large European river basins (3.1), a survey on the contamination sources and distribution patterns of pharmaceuticals and personal care products in a large Alpine river basin (3.2) and the calibration and application of a novel transport model of micro and emerging pollutants (3.3).

– Chapter 4 finally draw the conclusions of the main research topics presented in the previous chapters.

In detail, in the first part of this thesis, we provided a review of the "state-of-art" of water quality in surficial waters of three large European river basins among the six included in the GLOBAQUA project [136]. The selection of these basins was realised according to differences in hydro-climatic conditions and land use management, and to their contrasting resilience to climate change. The description of the studied basins is presented in Sec. 2.1. Particular attention was drawn to the Adige River, selected as study site for most of our analyses. An accurate decription of the three watersheds and their main stressors was presented, beliving that a detailed analysis of existing information is useful and necessary to identify the main stressors that may play in synergy. Moreover, we explored the complex interaction between water quality trends and the main stressors (from now on also called as drivers) observable at large scales and influencing the quality of surficial waters, by analysing whether observed changes are consistent with their drivers. From this part, we published a review article [39] and two papers [53, 116] in a top journal in the field of science and engineering .
In the second part of this thesis, informed about the general chemical status of surficial waters of the Adige River Basin, we presented and described the experimental activities designed within the GLOBAQUA framework in our study basin, the Adige catchment. Among the classical physico-chemical parameters, special attention was also given to emerging pollutants, whose study on the occurence patterns and spatio-temporal variability, limited to our main experimental study basin (i.e., Adige River Basin) was conducted in conjunction with population patterns and touristic fluxes. In particular we aimed at defining the

occurrence patterns of contaminants in relation to their sources (tourist arrivals, resident population), and at relating the temporal variability (summer-winter) of pharmaceuticals and personal care products (PPCPs) to the varying environmental variables (water flow, temperature), in water and sediments. From this part, we published two papers [102, 119].
Finally, in the third and last part of the thesis we defined a new parsimonious, in term of parameters, in-stream transport model which includes and counterbalances the simultaneous effects of dilution, dispersion and decay of pharmaceuticals in surface waters. As a validation, the model is applied to the main pharmacological classes of our main study cacthment, the Adige River Basin. Two manuscripts describing these methodology and with some applications are in preparation.

1.1 Data analysis of existing water quality variables of European rivers

The ecological and chemical status of freshwater has attracted significant attention in the last decades (e.g.,[4, 185]). Water bodies hosting important ecosystems are subject to anthropogenic and climatic stressors often acting in synergy. In order to estimate the effects of these actions aiming at improving the ecological status of freshwater ecosystems, monitoring networks have been implemented in the majority of European basins, providing a quite extensive database of water quality parameters [21]. Despite this wealth of data, the connection between the main drivers and water quality parameters has not been fully studied and deeply understood. Little is known beyond the effects of single stressors on the chemical and ecological status of water bodies and on their ecosystem functionality [136]. This lack of knowledge limits our

capability of understanding ecosystem responses to multiple stressors [64], and as a consequence, the possibility for water and land use managers to determine suitable adaptive strategies for mitigating their effects. Many studies described observed changes in chemical, ecological or hydrological variables (e.g., [27]), but few studies attempt to attribute causes of pattern variations [112]. Other works attempted to explain concentration patterns by using measurements of single experimental sampling campaigns without considering long temporal variations (e.g.,[102]). Moreover, few studies evaluated long-term trends in water quality indicators at single gauging stations or detect alterations in the spatial patterns, chiefly because of data fragmentation and sampling discontinuity [108, 189]. In this first part of the present thesis, we explores the complex interplay between water quality trends and the main drivers discernible at large scales and affecting surface water quality, by analysing whether observed changes are consistent with the drivers of change. To this aim, three large European river basins among the six included in the GLOBAQUA project [136] are studied: Adige, Ebro and Sava. The selection of these basins is made according to differences in hydro-climatic conditions and land use management, and to their contrasting resilience to climate change [116]. The main objectives of the first part are:

(i) analysing long term water quality trends in each selected river basin;

(ii) identifying links between observed patterns of physico-chemical variables and their drivers of change (i.e., agriculture, streamflow, air temperature and resident population) in each selected basin, through quantitative analyses;

(*iii*) comparing the studied basins with respect to their vulnerability and resilience to the identified drivers of change.

1.2 Contamination sources and distribution patterns of pharmaceuticals in the Adige River Basin

Beyond the analysis of the classical measured physico-chemical water parameters in rivers, it is worth including and analysing also solute emerging pollutants, whose concentrations in the environment are of increasing concern. With this term, we include synthetic or naturally occurring chemicals, not commonly monitored in the environment but which have the potential to enter the acquatic environment and cause known or suspected adverse ecological and human health effects. The term "emerging" is also used to describe not the pollutant itself, but rather a new "emerging concern", i.e., newly demonstrated toxic effect and/or mechanism of action of an old pollutant [19]. They are categorised into more than 20 classes related to their origin. The prominent classes are: pharmaceuticals, personal care products (PPCPs) (i.e., prescription drugs, non-prescription drugs, veterinary drugs and consumer chemicals typically found in fragrances, sun-screen agents, lipsticks, shampoos, hair colors and cosmetic products [28, 49]), pesticides, disinfection by-products wood preservation and industrial chemicals. In particular, PPCPs are considered emerging contaminants and can enter the aquatic ecosystem through multiple pathways, including human excretion, unused drugs and products, agricultural and livestock practices [28, 95, 141, 160, 179]. However, the main pathway for PPCPs to freshwaters is through wastewater effluents as a result of incomplete removal in the

wastewater treatment [71, 87, 176]. Because of this continuous release into the aquatic environment, PPCPs may act as pseudo-persistent contaminants [59], and as such may cause undesired and unexpected effects on the living organisms and environment [50, 61, 63, 174].

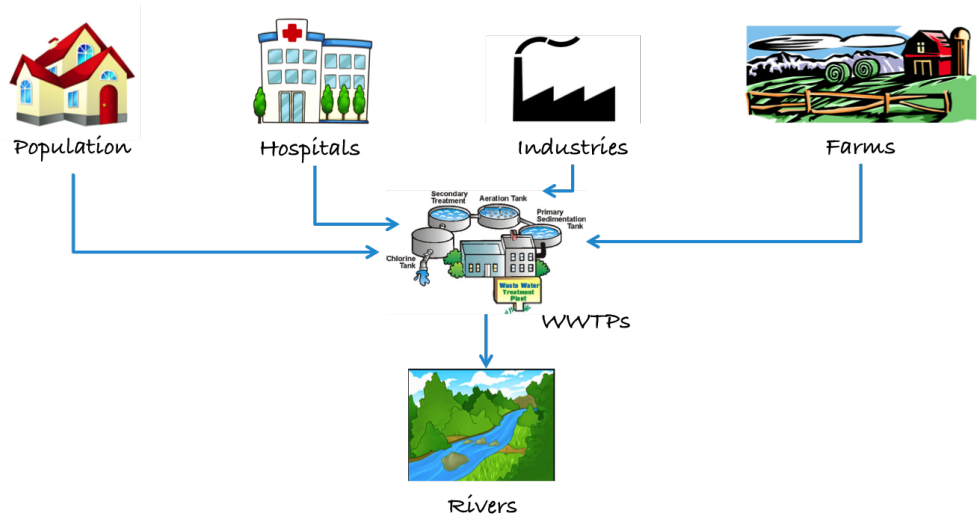

Figure 1.1: *Main sources of micro and emerging pollutants (i.e., pharmaceuticals and personal care products) in the aquatic ecosystem.*

PPCPs in the aquatic environment have been recognized as one of the most urgent environmental issues during the last decade [94]. Concentrations of PPCPs range from ngL^{-1} to μgL^{-1}, while their occurrence in water varies across different regions and seasons [98, 130, 173]. Moreover, the relevance of PPCPs associated with touristic activity in Alpine ecosystems is largely unknown. So far, the impact of tourism on river water quality has mostly been approached through the monitoring of the physicochemical and microbiological parameters [9, 23]. Even though several studies have reported concentrations of PPCPs in large rivers [127], papers regarding the occurrence of PPCPs in the Alpine streams are limited in number (see e.g., [151]. Therefore, the potential environmental threats to the aquatic environment associated with touristic fluxes and PPCPs in the

Alpine regions requires further investigation. In this context, our experimental catchment, the Adige River Basin, may be considered a representative basin with intense touristic activity both in summer and winter months. As a consequence, strong seasonality on consumption and use of PPCPs and their drain to the river system is likely to be expected. Waste water treated effluents have been identified as the main sources of contamination in the Adige catchment, while extensive hydropower exploitation [194], which has induced significant alterations of the streamflow regimes in both the main stem and tributaries [117] is likely to enhance the sensitivity of the river ecosystem to PPCP loads. Therefore, the present study aims at:

(i) defining the occurrence patterns of contaminants in relation to their sources (tourist arrivals, resident population);

(ii) relating the temporal variability (summer-winter) of PPCPs to the varying environmental variables (water flow, temperature), in water and sediments.

The mathematical framework at the basis of this analysis is described in Sec. 2.3.1, while the results are presented in Sec. 3.2.

1.3 Catchment scale transport model of micro and emerging pollutants

The presence of pharmaceuticals in the environment has posed a wealth of attention in the last decades, as these non regulated emerging contaminants are not frequently monitored but often detected in fresh waters in the range of nanograms to micrograms per litre [2, 59, 104, 152]. It is a common knowledge that the main route of entry of pharmaceuticals as well as human-use personal care products (PPCPs) into the aquatic environment is waste water treatment plants (WWTPs), whose

removal efficiency is dependent on the treatment processes and technology [75, 145, 156]. Owing to the concurrent effects of the increase in the use of drugs, often due to an increase in population and an improvement of health conditions, and the low pharmaceuticals removal efficiency of wastewater treatment plants, ubiquitous concentrations of pharmaceuticals in fresh waters have been detected. Possible consequences on the health of humans and of aquatic organisms have become issues of increasing concern by the scientific community worldwide [28, 85, 165]: disruption of human endocrine functions, developmental defects in fish and other organism, alterations in the survival, growth, and reproduction of a species, and the promotion of antibiotic resistance are just few examples [30, 40, 83]. For those reasons, the European Union, through the Directive 2013/139/EU, attempted to prevent the diffusion of pharmaceuticals in the aquatic environment by defining environmental quality standards and by pinpointing priority substances that could represent a potential risk. Furthermore, attempts to evaluate predicted concentrations in fresh waters have been made through many emerging contaminant models, among which the two most widely applied GIS-based models are PhATE (Pharmaceutical Assessment and Transport Evaluation [11]) and GREAT-ER (Geography-Referenced Regional Exposure Assessment Tool for European Rivers [60]). In order to be applied and corroborated, the two models need a huge amount of data in field conditions often difficult to obtain in field studies or in non-instrumented large basins [77]. It is well known that when modeling emerging contaminants the available information is limited and, therefore, simpler models are usually more useful than complex ones [7]. Nevertheless, more refined and higher tiered models will presumably result in more accurate predictions, but will require larger amounts of higher quality

data and more computing time [60]. Moreover, spatial consumption variation through population, due to differences between resident population and transient (i.e., tourist fluxes) is still missing [8]. In fact, very few studies have analyzed temporal and seasonal variations [47, 114, 157] in both predicted concentrations and in the estimation of the decay constant, both linked with touristic fluxes. The study of the fate and transport of pharmaceuticals in rivers, especially in catchments subject to significant touristic fluxes, which may induce fluctuations in the contaminant load, is in its infancy [43]. For those reasons, there is still potential for further development of emerging contaminant models and there is still the necessity of complementing the applications with measured data [7]. Within this framework, the core of the present thesis aims at

(*i*) defining a new parsimonious, in term of parameters, in-stream transport model which includes and counterbalances the concurrent effects of dilution, dispersion and decay of pharmaceuticals in surface waters.

(*ii*) applying the proposed transport model to the main pharmacological classes in a large Alpine river basin.

Its strength is that the only source needed to model pharmaceuticals is represented by human resident population and touristic fluxes when present, the latter varying seasonally, both considered as a proxy of the sewage effluents. Human population and touristic fluxes data are easily available and this let the model be applied to every catchments even large and non-instrumented, overcoming the lack of data. Moreover, the model can be easily coupled with existing hydro-climatological models to predict streamflow and water temperatures in ungauged basins, considering both steady and transient state. As a validation, the model is applied to the main pharmacological

classes of a large Alpine catchment (i.e., the Adige River Basin). The mathematical framework at the basis of this analysis is described in Sec. 2.3.2, while the results are presented in Sec. 3.3. Two manuscripts describing this methodology and the following application are in preparation.

CHAPTER 2

STUDY BASINS, DATA AND METHODS

2.1 Study basins

The Adige River Basin The Adige river rises from a spring in proximity of the Resia lake at the elevation of 1,586 m a.s.l. and after 409 km it ends in the Adriatic sea at Porto Fossone between Brenta estuary and Po river delta. With a contributing area of 12,100 km^2, the Adige is the third largest Italian river (after Po and Tiber) and the second longest (after Po). The mean water discharge registered at Boara Pisani gauging station (in the proximity of Rovigo municipality, near the catchment outlet) is about 202 m^3/s [52], with peaks usually registered in the period from June to September [146], showing the typical behavior of Alpine catchments.

The Adige river flows through the territories of the Province of Bolzano (62% of the overall river basin surface), the Province of Trento (29%) and the Veneto region (9%). From the source to Merano the Adige flows east through the Venosta valley (with a drainage area of 1,680 km^2). Then, it turns south and crosses the

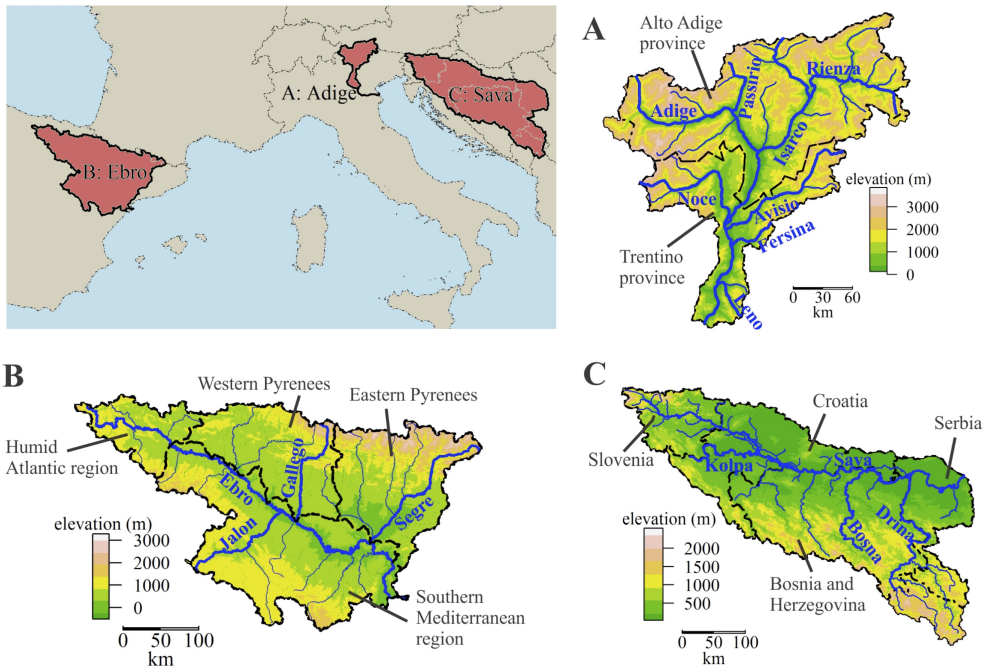

Figure 2.1: *Map presenting the locations of the study river basins: A) Adige B) Ebro and C) Sava with main regions and tributaries. Digital elevation models (DEMs) are also presented as coloured maps.*

valley that holds its name. The Adige receives the contribution of the Isarco river, close to Bolzano, and the contributions of both the Noce and Avisio rivers just upstream of Trento, where the drainage area of the Adige river rises, thanks to these contributions, to 9,810 km^2. Finally, it crosses the Lagarina valley until Verona (drainage area of 11,100 km^2) and then it turns east again and flows through the Padana plain without receiving other significant contributions. Because of the lack of significant contributions in the lower reach, hydrological studies have been conducted chiefly in the northern part of the catchment (i.e., Province of Trento and Province of Bolzano). The river basin is divided into 7 main subbasins: Passirio, Isarco-Talvera, Rienza, Noce, Avisio, Fersina, Leno (see Figure 2.1A). In particular, the Noce River is one of the main tributary of the Adige main stem. With a length of 82 km and a total contributing area is of 1,367 km^2, it rises from the reliefs of the

Ortles-Cevedale and Adamello Presanella groups and flows first to East, but in its middle course it turns to South-East and enters the river Adige close to the municipality of Mezzolombardo a few kilometers North of the city of Trento [117]. The Adige river basin contains 550 lakes, most of which have a surface smaller than 1 ha and of glacial origin [15]. The biggest natural lake is Caldaro, followed by Anterselva, Braies and Carezza in the Province of Bolzano, Lake Tovel and Terlago in the Province of Trento.

The Ebro River Basin The Ebro River Basin is mainly located in the north-eastern part of Spain (Figure 2.1B). With a catchment area of 85,362 km^2 , the Ebro is the largest river basin of Spain. The basin extends from the Pyrenees and the Cantabrian Range in the north (maximum altitude of more than 3,000 m a.s.l.) to the Iberian Range in the South and the Coastal Range in the East [112]. The Ebro River has a length of 910 km and it drains into the Mediterranean Sea with a mean streamflow of 425 m^3/s. Segre, Cinca, Aragón, Gallego, Jalon and Zadorra are the main tributaries of the Ebro River. Long-term mean annual air temperature is 11.4 $°C$ and mean annual precipitation is 620 mm (both evaluated in the time span $1920-2000$; [161]. The climate is mostly continental-Mediterranean, since it ranges from semi-arid in the centre of the river valley to oceanic in the Pyrenees and Iberian Mountains.

The Sava River Basin The Sava River Basin is located in the southern part of the Danube Basin (Figure 2.1C) and it drains into the Black Sea. With a catchment area of 97,713 km^2, the Sava is the second largest tributary of the Danube after the Tisza River. Altitude ranges from 71 m a.s.l. at the catchment outlet to 2,778 m a.s.l. in the Slovenian alpine headwaters [171]. The Sava is a transboundary river and its basin encompasses 6 countries: Slovenia (11% of the total catchment area), Croatia (26%), Bosnia

and Herzegovina (40%), Serbia (15.4%), Montenegro (7.5%), and a minor portion in Albania (0.1%). It is 945 km long and it drains into the Danube in Belgrade (Serbia). Climatic conditions along the river course range from alpine to continental. Long term annual mean temperatures, evaluated between 1971 and 2000, range from 6 $^{\circ}C$ in the mountain regions to 13 $^{\circ}C$ close to the river mouth [139]. Mean annual precipitation, evaluated between 1961 and 1990, ranges from 800 mm to 1,600 mm [140].

2.2 Data

As anticipated in the introductory chapter, in the first part of the present thesis, we performed a complete data analysis of both surficial water quality variables obtained mainly from the Environmental protection agencies and existing hydro-climatological data, by using advanced statistical tools. To this aim, we compared the three European river basins presented in Sec. 2.1. Data used for these first parts are described in Sec. 2.2.1. For the second part of the thesis, the description of the experimental activities performed in the Adige catchement is provided in Sec. 2.2.2, whereas data used in the last parts of the thesis, for the application of the transport model to the Adige catchment, are presented in Sec. 2.2.3.

2.2.1 Existing water quality variables

For reasons of comparability between the three basins, the study period was set from 1990 to 2015: restriction to the time frame was necessary because of the limited availability of measurements for some variables in the Sava and Adige basins and the availability of Corine Land Cover information [58], which is available only since 1990. As suggested by [88], only those stations with long records (i.e., at least 24 measurements

during the study period) were considered in all the three basins to perform trend analyses. Data were organised into two groups: variables and drivers. The former included water quality data used to detect the trends, while the latter included selected important factors available continuously in time at the European scale, i.e., instantaneous and monthly aggregated streamflow, monthly aggregated air temperature, population density and percentage of agricultural land use. The percentage of artificial areas such as "urban fabric", "industrial, commercial and transport units", "mine, dump and construction sites" and "artificial, non-agricultural vegetated areas" (cf. Corine Land Cover class information), was discarded from the analysis due to the similarity in the spatial patterns with population density. Hence, the driver population density was assumed as an indicator of the overall anthropogenic impact. Other determining features were not included in the statistical analyses because of the difficulty to obtain them at monthly time scale and for all the investigated catchments. These include treated and untreated waters, livestock density, industrial outflows, mining activities, crop choices, and intensity of agricultural production, which may be considered in future studies at smaller scales (e.g., specific regions of large river basins). Nevertheless, annual data of livestock and phosphate fertilisers for the three basins were used in order to support the discussion. Data were downloaded from the Italian institute of statistics (ISTAT, *http*: *//agri.istat.it/sag_is_pdwout/jsp/Introduzione.jsp*, 2016) for the Adige basin and from the Food and Agriculture Organization of the United Nations (FAOSTAT, *http*://*www.fao.org/faostat/en/data/*, 2015) for the Ebro and Sava basins. In detail, for the Adige basin, information on phosphate fertilisers and livestock are available in the periods

2003 – 2015 and 2002 – 2016, respectively, but aggregated at regional scale, which is wider than the Adige catchment of about 3,000 km^2. For the Ebro, the data refer to the whole area of Spain. Phosphate fertiliser data are available for the period 2002 – 2014 and livestock data for the period 1990 – 2014. Finally, for the Sava, data are aggregated at each national scale (i.e., Croatia, Serbia, Montenegro, Slovenia, and Bosnia and Herzegovina) over periods that vary depending on the country. For phosphate fertilisers, the longest period is 2002 – 2014, while for livestock density, the longest period is 1992 – 2011 only for Bosnia and Herzegovina, Croatia and Slovenia.
Physico-chemical variables were available at monthly resolution at 45, 42 and 22 monitoring stations in the Adige (Figure 2.2A; http://www.appa.provincia.tn.it; http://www.provincia.bz.it/agenzia ambiente/), Ebro (Figure 2.2B; http://www.datossuperficiales.chebro.es:81/WCASF/) and Sava (Figure 2.2C; http://www.icpdr.org/wq-db/), respectively. The dataset used in this work includes only variables, selected from larger sets of parameters, that are in common among the three basins: pH, water temperature (TW), electrical conductivity (cond) and concentrations of arsenic (As), biological oxygen demand (BOD5), chemical oxygen demand (COD), dissolved oxygen (DO), total nitrogen (Ntot), phosphates (PO_4), total phosphorus (P_tot), chloride (Cl), suspended solids (SS) and sulphates (SO4). All variables are expressed in mg L^{-1} except pH [−], electrical conductivity [μScm^{-1}] and water and air temperatures [$°C$]. Dissolved oxygen as % saturation was not included in the present analysis due to the lack of complete time series. Concentrations below the detection limit were discarded prior to the analysis [88]. To test data consistency, Table 2.1 presents the main statistics of the available water quality data.

Table 2.1: *Water quality variables included in the study, mean values and ranges in the period 1990-2015.*

	Adige		**Ebro**		**Sava**	
	Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**
Arsenic (As)	$2.3E-04$	$5.7E-05-9.2E-04$	$7.3E-05$	$4.1E-05-3.2E-04$	$1.3E-04$	$5E-04-2.6E-04$
BOD5 (BOD5)	2	1.2 – 3.4	6.2	3.3 – 28	2.1	0.84 – 3.2
pH (pH)	8	7.3 – 8.6	8	7.5 – 8.3	8	7.5 – 8.3
Water temperature (TW)	8.4	5.4 – 13	13	9.6 – 18	15	11 – 19
COD (COD)	5.8	2.8 – 16	13	4.8 – 41	10	0 – 20
Dissolved Oxygen (DO)	11	8.6 – 12	10	8 – 11	9.9	7.8 – 12
Total Nitrogen (N_{TOT})	1.2	0.43 – 11	5.4	2.2 – 8.5	1.5	0.72 – 2.2
Phosphates (PO_4)	0.13	0.031 – 2.2	0.34	0.09 – 1.2	0.17	0.024 – 0.54
Total Phsphorus (P_{TOT})	0.066	0.01 – 0.85	0.11	0.034 – 0.34	0.095	0.02 – 0.19
Cloride (Cl)	4.3	0.88 – 36	63	6.6 – 330	17	2.4 – 150
Suspended Solids (SS)	46	2.5 – 180	35	4.2 – 170	16	0 – 35
Electrical Conductivity (cond)	230	92 – 550	680	93 – 2,200	390	240 – 700
Sulphates (SO_4)	32	1.9 – 190	160	71 – 1,200	18	7.5 – 27

Instantaneous streamflow time series (Q) were retrieved from the hydrological offices of the Provinces of Trento ($http://www.floods.it/public/index.php$) and Bolzano ($http://www.provincia.bz.it/hydro/index\_i.asp$) for the Adige, and the Confederación Hidrográfica del Ebro (CHE) for the Ebro. For the Sava, daily streamflow were obtained from the Global Runoff Data Centre portal (GRDC, $http://www.bafg.de/GRDC/EN/Home/homepage\_node.html$), the TransNational Monitoring Network (TNMN $http://www.icpdr.org/wq-db/$) and national water agencies of the countries crossed by the Sava (Environmental Agency of the Republic of Slovenia, ARSO, $www.arso.gov.si$; Hrvatske vode, $www.voda.hr$; and Republic Hydrometeorological Service of Serbia, $www.hidmet.gov.rs$). When streamflow is not available at the water quality monitoring station, it is inherited from the closest gauging station, after rescaling with the contributing area. However, if streamflow measurements are not available at all the available gauging stations in the same period of water quality sampling, or the closest gauging station is too far away, the respective concentrations are discarded prior to analysis [116]. Coupled with Q time series, monthly aggregated data (Q_m) were also introduced as a proxy of the seasonality of the hydrological cycle. Monthly time series of air temperature (TA) were extracted from the version 12.0 of the 0.25 [$°C$] resolution E-OBS gridded dataset [79] by selecting the temperature of the grid cells containing the sampling points. The dataset was downloaded from $http://www.ecad.eu$. Percentage of agricultural land use retrieved from Corine Land Cover (years 1990, 2000, 2006 and 2012; EEA, 2013) is assumed as an indicator of the impact of agricultural activities, whilst population is considered as a proxy of urban areas and the associated contaminant loads. Although

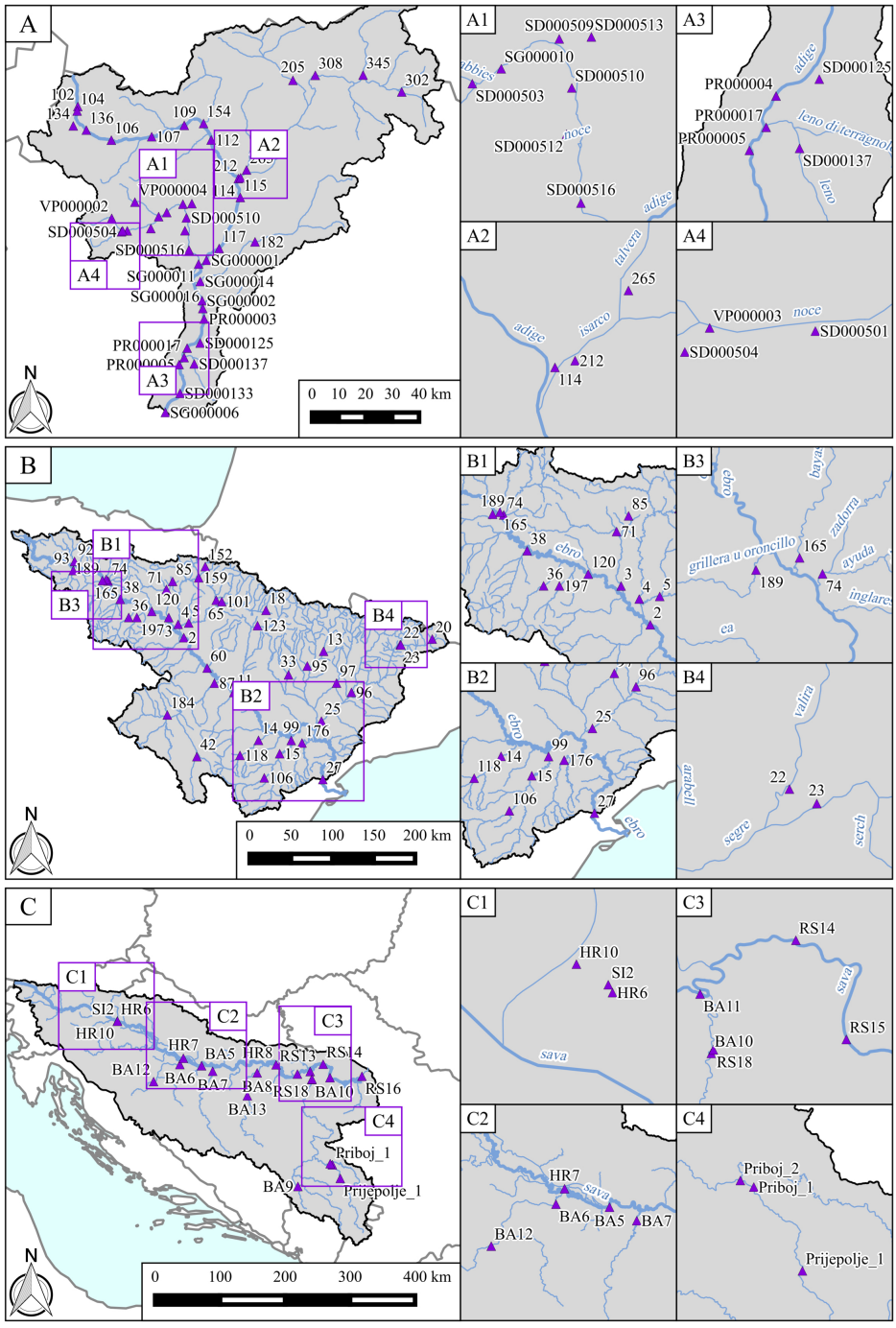

Figure 2.2: *Locations of water quality sampling stations for Adige (A), Ebro (B) and Sava (C), respectively. Identifiers refer to the original codes as retrieved from the case-specific water agencies. For the station codes see [53]. Right-side picture enlargements show regions with a high station density.*

a more detailed small-scale analysis of industrial activities, including mine production and agriculture, may provide additional insights, available data currently do not allow this type of analysis. Population data at an interval of 5 years from 1990 to 2015 were obtained from NASA Socioeconomic-Data-and-Applications-Center (downloaded from http://beta.sedac.ciesin.columbia.edu/data/collection/gpw-v4/sets/ browse, 2017). For each river basin, drainage areas at the sample locations were determined from the European-wide digital elevation model provided by the GMES RDA project (downloaded from http://www.eea.europa.eu/data-and-maps/data/eu-dem, 2017). Annual population and agriculture data were then aggregated at the level of the single sub-basin by linearly interpolating between the two closest years with information in the dataset.

2.2.2 Experimental sampling campaigns

Pharmaceuticals and personal care products (PPCPs) concentrations in the Adige River Basin were obtained during two extensive sampling campaigns performed in 2015 (February 15^{th} - 18^{th} and July 3^{rd} - 5^{th}, 2015) in twelve selected sites (see Figure 2.3). The list with the code, name and reasons of the selection is the following:

- WB1 (i.e.: 1): Bresimo in the Noce catchment. Reference site in almost pristine conditions;
- WB2A and WB2B (i.e.: 2A and 2B): downstream WWTP of the Tonale pass in the Noce catchment. Example of headwater with low water discharge at the Tonale pass impacted by the release of a WWTP;

- WB3A and WB3B (i.e.: 3A and 3B): downstream WWTP of Mezzana in the Noce catchment. Example of headwater impacted by both WWTP release and hydropeaking;
- WB4B (i.e.: 4B): downstream S. Giustina reservoir in the Noce catchment. Lower course of the Noce at Mezzocorona, downstream of two reservoirs in series, one with large capacity;
- WB5B (i.e.: 5B): downstream Mezzocorona power plant in the Noce catchment. Lower course of the Noce at Zambana, downstream WB4B and the restitution of a large hydropower plant;
- WB6B (i.e.: 6B): located in the main stem of the Adige at Faedo upstream the city of Trento and the main tributaries in the Trentino region (Noce, Avisio and Fersina);
- WB7A, WB7B, WB7C and WB7D (i.e.: 7A, 7B, 7C, 7D): four sites between Mattarello and Rovereto, downstream the city of Trento, in the Adige main stem. Example of headwater impacted by human activities.

For the sake of simplicity, the prefix "WB" (i.e. Water Body) in Figure 2.3 was omitted.
Sediment samples were collected with a small inox spade from the uppermost 10 cm sediment layer of both left and right banks and then mixed. Hence, they were sieved on site with a 2 mm mesh sieve. Samples were subsequently stored in high-density polyethylene (HDPE) ⊘ 88 1 L bottles. Liquid samples, taken on the top of the water level, were collected on the left, center and right river side and then mixed. Water samples for the analysis of pharmaceutically active compounds (PhACs) were stored in 1 L gray PE bottles, while water samples for the personal care products (PCPs) analysis were stored in 500 mL amber glass

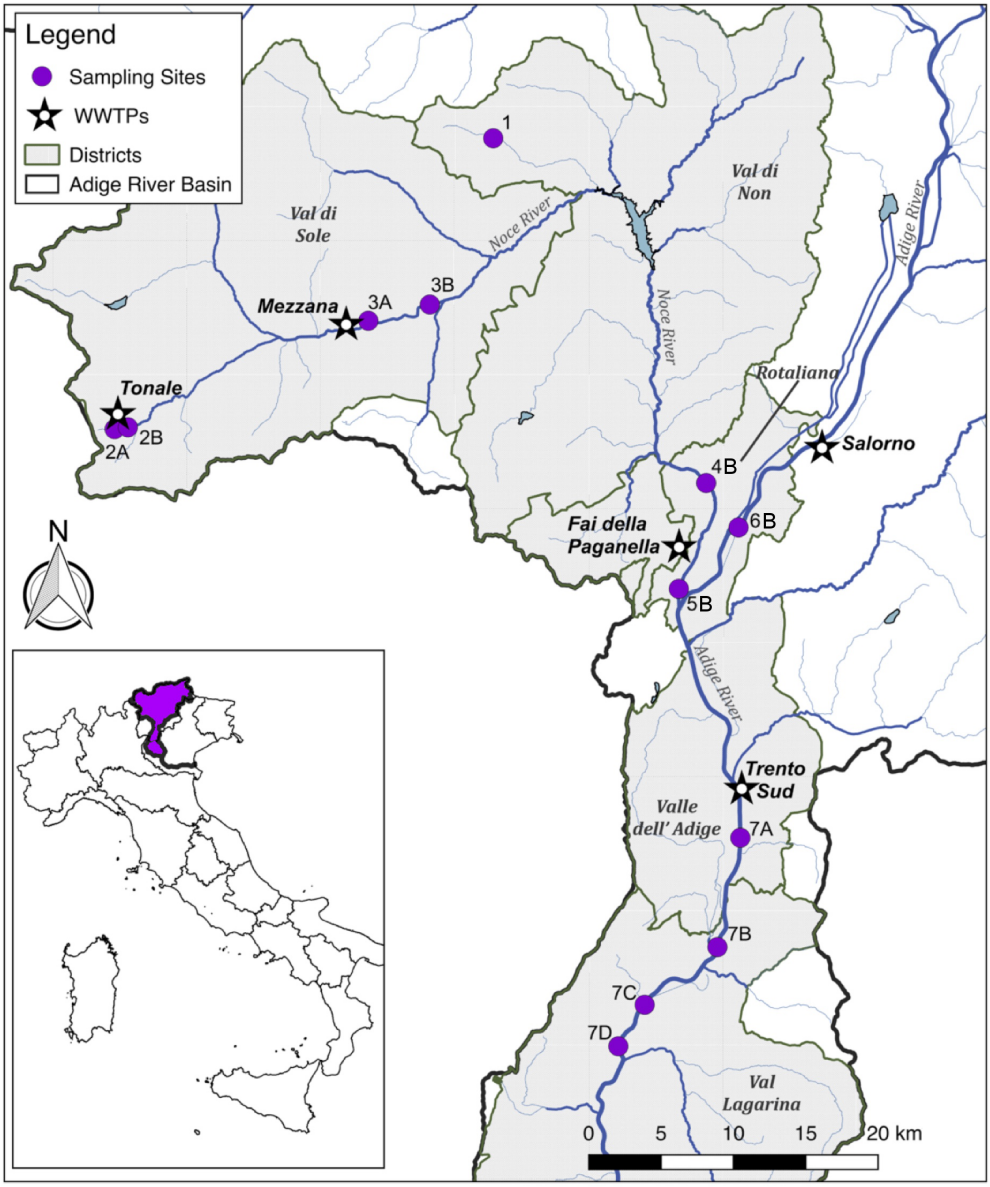

Figure 2.3: *Sampling sites (purple dots) in Adige river basin and the associated WWTPs (black stars). The bottom left inset shows the location of the Adige basin within the Italian territory. For simplicity, the prefix "WB" (i.e. Water Body) was omitted.*

bottles. Afterwards, samples were transported to the laboratory in a refrigerated isothermal container (dry ice) and stored at -20 $^{\circ}C$ until extraction. Water temperature and specific electrical conductivity at the standard temperature of 25 $^{\circ}C$ were measured with an Aquatroll 200 multi-parameter probe, while turbidity was measured by a Ponsel IR optical turbidimeter. River velocity was measured by a Decatur Electronics Europe Inc. radar gun 2016. Regarding sample preparations and analysis, all chemical standards used in this research were of high purity grade (> 90%). Following the preparation, standardswere stored on -20 $^{\circ}C$. Fresh stock antibiotic solutions were prepared every month due to their limited stability while the stock solutions for the rest of substances were renewed every three months. In particular, regarding the pharmaceutically active compounds (i.e., PhACs), the analysis in water samples was conducted following the method developed by [74]. The analyses were carried out with an off-line solid phase extraction (SPE) followed by ultrahigh- performance liquid chromatography coupled to triple quadrupole linear ion trap tandem mass spectrometry (UHPLC-QqLIT-MS2). Chromatographic separations were carried out with a Waters Acquity Ultra-Performance^{TM} liquid chromatography system, coupled to a 5,500 QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer (Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source. Moreover, the target analytes were eluted from the column into the chromatograph with the LC-mobile phase, and the separation was achieved with two binary pump systems (Milford, MA, USA), using an Acquity HSS T3 column (50 mm x 2.1 mm i.d., 1.8μm particle size) for the compounds analyzed under positive electrospray ionization (PI) and an Acquity BEH C18 column (50 mm x 2.1 mm i.d., 1.7μm particle size) for the ones analyzed under negative

electrospray ionization (NI), both purchased fromWaters Corporation. Electrospray Ionization (ESI) and the reaction monitoring (SRM) modes were selected for the MS2 detection. Prior to the instrument analysis, standard mixture containing all isotopically labeled standards was added in the extracts as an internal standard. Quantification was carried out by isotope dilution. The analysis of PhACs in sediment samples was carried out according to the method developed by [93]. Previously freeze-dried and homogenized sediment samples were extracted by pressurized liquid extraction (PLE) using an ASE 300 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA) equipped with 11 mL stainless extraction cells. The extracts of sediment obtained by PLE ($\sim 22mL$) were diluted in 500 mL of HPLC water (methanol < 5%) and processed by SPE using the Oasis HLB cartridges (200 mg, 6 mL). The resulting extracts were evaporated under a gentle stream of nitrogen and reconstituted with the internal standard solution to a final volume of 1 mL. The analyses of the samples were carried out by UHPLC-MS2 in the same analytical platform as for the water samples. The analysis of PCPs in water samples was conducted following the method developed by [67]. The analyses were carried out by on-line solid phase extraction-high performance liquid chromatography-tandem mass spectrometry (SPE-HPLC-MS2). The analyses were carried out on a Transcend LX System chromatograph with Equan^{TM}Technology coupled to a TSQ Vantage, both from Thermo Scientific (Sunnyvale, CA, USA). For the on-line SPE extraction on the Equan^{TM}, a column HyperSep PEP from Thermo Scientific was used. Five ml of water samples were infused through the column. Moreover, the target analytes were eluted from the column into the chromatograph with the LC-mobile phase, where the separation was achieved using a LiChroCART Purospher STAR RP-18 ec (125 mm x 2.0 mm i.d.,

5μm particle size) analytical column from Merck preceded by a guard column LiChroCART 4-4 Purospher STAR RP-18 ec (5μm particle size). Atmospheric Pressure Photo- Ionization (APPI) and SRM modes were selected for the MS2 detection. Before the instrument analysis, a standard mixture containing all isotopically labeled standards was added in the extracts as an internal standard. Quantification was carried out by isotope dilution. PCPs in sediment samples were determined according to the method by [66], using frozen-dried and homogenized samples. After the addition of the surrogate standards to the samples, the target analytes were extracted by PLE in an ASE-350 Accelerated Solvent Extractor (Thermo Fisher Scientifics). The resulting extracts were brought to 25 mL with MeOH and aliquots of 2 mL were then filtered using a 0.45μm nylon syringe filter into LC-vials. These solutions were allowed to evaporate under a gentle stream of nitrogen and reconstituted with the internal standard solution to a final volume of 1 mL. The analyses of the samples were carried out by HPLC-MS2 in the same analytical platform as for the water samples, disabling the on-line configuration. Other experimental conditions were the same as those for water analysis.

2.2.3 Data for transport model

Pharmaceuticals concentrations in the Noce sub-basin were obtained during the same two extensive sampling campaigns performed in 2015 described in the previous section. We decided to include in the model calibration only the five selected sites that belong to the Noce catchment, excluding both the site WB1 at Bresimo for the low concentrations detected and the four sites downstream the municipality of Trento because of the high unceirtanties associated with the souces of pharmaceuticals. The sites included in the application of the model transport are

the following (see Figures 2.3 - 2.4, [119]): WB2B - downstream WWTP of the Tonale pass, WB3A and WB3B - downstream the WWTP of Mezzana, WB4B - downstream S. Giustina reservoir and WB5B - downstream Mezzocorona power plant Among the measured pharmaceuticals, a subset of only 5 compounds was selected for the application of the transport model with the criteria of the highest concentrations in both the sampling campaigns. The only exception is Diclofenac, which was detected only in Febraury sample but it was included because it belongs to the "watch list" of 2013/39/EU. The 5 pharmaceuticals are the following (https://pubchem.ncbi.nlm.nih.gov/compound):

- Diclofenac: non-steroidal anti-inflammatory drug with antipyretic and analgesic actions;
- Ketoprofen: non-steroidal anti-inflammatory drug, analgesic and antipyretic;
- Clarithromycin: semisynthetic macrolide antibiotic;
- Sulfamethoxazole: sulfonamide bacteriostatic antibiotic. Its broad spectrum of activity has been limited by the development of resistance;
- Irbersartan: nonpeptide angiotensin II antagonist with antihypertensive activity.

Regarding the first-attempt values of the two parameters in the model considered for calibration, the theoretical load coefficient (γ_i) was estimated through the available data from WHO Collaborating Centre for Drug Statistics Methodology (World Health Organization; http://www.whocc.no/) and AIFA (Agenzia Italiana Far-maco;https://farmaci.agenziafarmaco.gov.it/bancadatifarmaci/home.).

First-attempt estimation of the coefficient of decay (k_i) were performed through previous available studies.
Location of WWTPs were obtained from Agenzia per la Depurazione of the Province of Trento (https:// adep.provincia.tn.it/Agenzia-per-la-Depurazione-ADEP) and from Province of Bolzano (http: // www.provincia.bz.it/agenzia-ambiente/acqua/cartine-schede.asp for Alto Adige Province). The distances between each WWTP and the measuring points were defined through QGIS, an open source Geographic Information System (http://www.qgis.org/it/site/).
Resident population and tourist presences were obtained from the census offices of Trento http://www.istat.it/it/ and https://astat.provincia.bz.it and Bolzano, for the territories of the two provinces. Resident population is considered constant for each year while tourist presences are subject to monthly fluctuation. Both were assigned to each WWTP: according to the municipality served, population data were therefore aggregated.
Daily streamflow time series (Q) were retrieved from the hydrological offices of the Provinces of Trento ($http://www.floods.it/public/index.php$) and Bolzano ($http://www.provincia.bz.it/hydro/index_i.asp$). For the application at the catchment scale, monthly time series were obtained through aggregation of daily streamflow values.
Water temperatures (WT) were provided by the Environmental Protection Agencies of the provinces of Trento (http://www.appa.provincia.tn.it) and Bolzano (http://www.provincia.bz.it / agenzia-ambiente/) at monthly resolution (Figure 2.4).

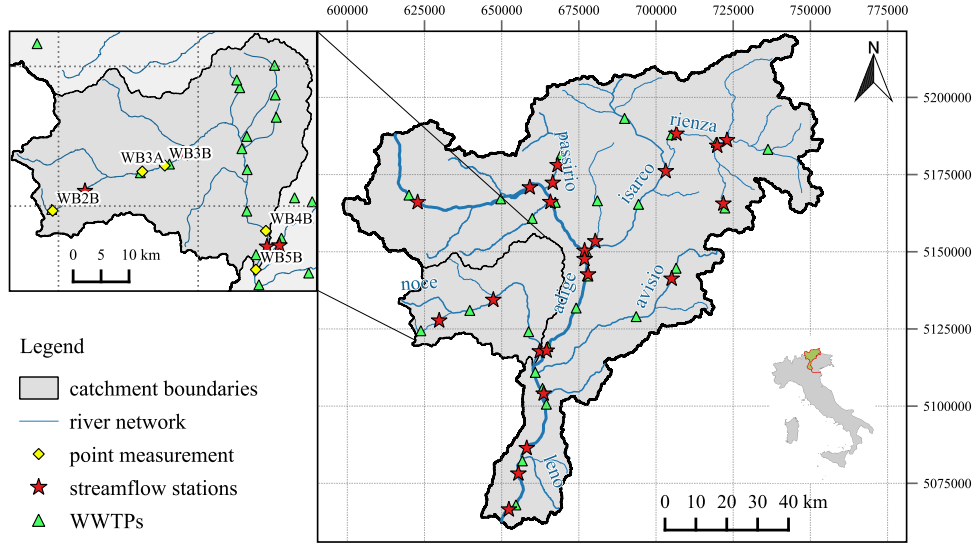

Figure 2.4: *Map of the Adige River basin and its main tributaries with a zoom of the Noce River basin (upper panel). Green triangles represent the main WWTPs whereas red stars the main streamflow gauging stations. Only for the Noce basin, yellow diamonds symbolize point measurements of the two sampling campaigns (i.e., February and July 2015).*

2.3 Methods

2.3.1 Statistical analyses

In order to analyse long term water quality trends in the selected river basin and to identify the links between their observed patterns and some hypotetical drivers of change, multiple statistical tools have been applied to the available time series, such as Spearman rank correlation, Principal Component Analysis and Mann-Kendall trend test. The Spearman rank correlation [172] was calculated to preliminarily estimate the level of correlation between the physico-chemical parameters and drivers. Spearman's R is a special case of the Pearson coefficient in which the data are converted to ranks before calculating the correlation coefficient [27]. The Spearman rank correlation was performed between all pairs of variables and drivers at each station for the three basins. Subsequently, mean

R coefficients were calculated in order to identify correlations as general descriptors of the interplay between water quality parameters and drivers. Principal Component Analysis (PCA) is a powerful technique of multivariate data analysis useful for identifying patterns in data [167, 190]. In the present work, PCA was applied separately to the complete dataset (both variables and drivers) of each study basin in order to screen temporal and spatial patterns and to select meaningful synthesis variables facilitating the ensuing analyses. PCA was also used to validate the results of Spearman rank correlation, with the further advantage of encompassing spatial information. Since water quality data follow skewed distributions, trend analyses were performed with the nonparametric Mann-Kendall (MK) test in all river basins [99, 120]. The MK-test does not require a priori assumptions of the underlying distributions and should be preferred to parametric trend tests in the analysis of multiple datasets [88]. In order to calculate the sign and magnitude of trends, Sen's slope estimator was determined from the MK-statistics because it does not require the underlying probability distribution to be Gaussian and it is less sensitive to outliers than the Ordinary Least Square [166]. The statistical significance of trends is defined using a significance level of $\alpha = 0.1$ for Kendall's p-value. MK trends and Sen's slope estimator were computed for time series of water quality variables with at least 24 measurements. All statistical and graphical analyses were performed using R statistical software packages ($https://www.r-project.org$).
Regarding the statistical analyses performed in the second part of the thesis, preliminary data analyses to explore the relationship between PPCP levels and their drivers (i.e., tourist arrivals, resident population) were performed by calculating Pearson moment correlation factor (r) [149]. We used the sum of

compounds in each family for each sampling location to perform pairwise correlation with the tourist arrivals (February and July 2015), and the resident population in each municipality. Pairwise correlations were performed for water and sediment samples. For each calculated probability (p), the significance threshold was set at 0.05.

2.3.2 Transport model: mathematical framework

In the following, we present the mathematical framework developed for the definition of a novel transport model for pollutants in surficial waters. Firstly, we introduce the general catchment scale transient model, and then we applied the steady state version to model pharmaceuticals in the Adige River Basin. The steady state model inherits the same mathematical framework of the transient one but introducing some assumptions and semplifications.

General transient model Let us consider a parcel of water traveling from its entry point in the hydrological system, the source, and a compliance plane, containing the position where it is detected. The parcel contains an initial mass Δm_0 of a reactive solute which is transported within the hydrological system and may undergo chemical transformation. Under this hypothesis, transport can be modeled by the following governing equation:

$$\frac{\partial C_r}{\partial t} = \frac{\partial}{\partial \xi}\left[\alpha_L\, v(\xi,t)\frac{\partial C_r}{\partial \xi} - v(\xi,t)\, C_r\right] + R(\xi,t) \qquad (2.1)$$

where C_r $[M/L^3]$ is the solute concentration, ξ $[L]$ is the Lagrangian coordinate measured along the particle's trajectory, t $[T]$ is time, v $[L/T]$ is the magnitude of the velocity field, α_L $[L]$ is the longitudinal dispersivity, and R is the sink/source term representing chemical reaction. Equation (2.1) is the classic local

Reactive Advection Dispersion Equation (RADE) written in an orthogonal coordinate system moving with the solute's particle (see e.g. [17]), where we neglected diffusive flux transverse to the trajectory line [123].
We assume now that the velocity can be approximated as follows:

$$v(\xi, t) = v_0(\xi)\,\phi(t) \tag{2.2}$$

where v_0 is the velocity in a reference stationary state and ϕ describes the non-stationary effect introduced by the boundary conditions. A similar hypothesis was introduced in the work by [170]. This class of velocity fields has the property that the trajectory of the particle does not change in time, since it is dictated by v_0, while the change in the velocity caused by changes of boundary conditions propagates instantaneously along the entire trajectory. This type of velocity field, is mathematically convenient and it is consistent with the Instantaneous Unit Hydrograph theory based on the width function, which assumes that flow moves along a fixed drainage network dictated by topography [121]. Nevertheless, steady-state approximation does not entail that the transport velocity can be spatially constant. In order to implement this refinement, we also introduce the assumption that the velocity varies spatially according to the following power law expression proposed by [107]:

$$v_p = \Phi(A)\,Q_p^{\Psi(A)} \tag{2.3}$$

expressing the $p-$th quantile of the velocity v_p $[m\,s^{-1}]$, as a function of the same quantile of water discharge Q_p $[m^3\,s^{-1}]$. In Equation (2.3), A $[km^2]$ is the contributing area and Φ and Ψ are scaling coefficients, which do not depend on the chosen

quantile. The expressions of Φ and Ψ provided by [54], by using a dataset of 85 gauging stations in Kansas and Oklahoma, were calculated by the following expression:

$$\Phi(A) = \exp\left[-\left(\alpha_{C_A} + \beta_{C_A} ln(A)\right) + \left(\alpha_Q + \beta_Q ln(A)\right)\Psi_{C_A}\right] \quad (2.4)$$

with

$$\Psi_{C_A}(A) = \left[\frac{\gamma_{C_A} + \delta_{C_A} ln(A)}{\gamma_Q + \delta_Q ln(A)}\right]^{1/2} \quad (2.5)$$

and finally the exponent Ψ is given by:

$$\Psi(A) = 1 - \Psi_{C_A}(A) \quad (2.6)$$

In all these expressions A $[km^2]$ is the contributing area and the other coefficients are reproduced in the table 2.2 (see also Table 3 of the paper by [54]).

Table 2.2: Coefficients for the definition of Ψ and Φ.

Hydraulic geometry factors	α	β	γ	δ
C_A	−3.1802	0.6124	0.8404	0.1130
Q	−5.5428	0.7992	2.6134	0.0012

The expression (2.3) is a generalization of the power law expression $v \propto Q^m$ introduced in the pioneering work of [107], who noticed that the exponent m varies in dependence of the contributing area. Under the commonly accepted approximation that at the network scale the contributing area increases stepwise at the nodes of the network, we assume the velocity spatially uniform within the channels. However, preliminary comparative analyses of the two velocities (see Eq. 2.2 and Eq. 2.3) evidenced similar results (in terms of simulated concentrations) of the model.

By substituting the expression (2.2) into Equation (2.1) we obtain:

$$\frac{\partial C_r}{\partial t} = \phi(t)\,\frac{\partial}{\partial \xi}\left[\alpha_L\, v_0(\xi)\frac{\partial C_r}{\partial \xi} - v_0(\xi)\, C_r\right] + R(\xi, t) \tag{2.7}$$

We limit here to the biogeochemical reaction which can be represented as an irreversible first order decay of the type $R(\xi, t) = -kC_r(\xi, t)$, where the first order decay rate may be both positive, in case of degradation occurring in the liquid phase, and negative, in case of solute dissolution from the solid matrix. In the latter case dissolution is not rate limited [109]. Equation (2.7) can be transformed in the ADE for a passive solute by introducing the following transformation:
$C_r(\xi, t) = C(\xi, t)\,\exp[-k\,t]$,

$$\frac{\partial C}{\partial t} = \phi(t)\,\frac{\partial}{\partial \xi}\left[\alpha_L\, v_0(\xi)\frac{\partial C}{\partial \xi} - v_0(\xi)\, C\right] \tag{2.8}$$

where C $[M/L^3]$ is the concentration of a passive tracer sharing the same trajectory with the target reactive solute.
By introducing the following transformation: $T = \int_{t_0}^{t} \phi(t')\,dt'$, where t_0 is the time at which the particle has been injected into the system, we obtain:

$$\frac{\partial C}{\partial T} = \frac{\partial}{\partial \xi}\left[\alpha_L\, v_0(\xi)\frac{\partial C}{\partial \xi} - v_0(\xi)\, C\right] \tag{2.9}$$

We introduce now the travel time:

$$\tau = \int_0^{\xi} \frac{d\xi'}{v_0(\xi')} \tag{2.10}$$

which substituted into Equation (2.9) leads to:

$$\frac{\partial C}{\partial T} + \frac{\partial C}{\partial \tau} = \frac{\alpha_L}{v_0(\tau)} \frac{\partial^2 C}{\partial \tau^2} \tag{2.11}$$

By introducing the hypothesis $v_0(\tau) = v_0 = constant$, Eq. (2.11) becomes:

$$\frac{\partial C}{\partial T} + \frac{\partial C}{\partial \tau} = \frac{\alpha_L}{v_0} \frac{\partial^2 C}{\partial \tau^2} \tag{2.12}$$

After introducing the following characteristic time $t_a = L_0 / v_0$, where $v_0[L/T]$ is the mean velocity and L_0 is a characteristic length of the hydrological system, the transport equation (2.12) becomes:

$$\frac{\partial C}{\partial T^*} + \frac{\partial C}{\partial \tau^*} = \frac{1}{Pe} \frac{\partial^2 C}{\partial \tau^{*2}} \tag{2.13}$$

where, $Pe = L_0 / \alpha_L$ is the Peclèt number. In Equation 2.13 $T^* = T\, v_0 / L_0$ and $\tau^* = \tau\, v_0 / L_0$ are the dimensionless time and travel time, respectively. The solution of the equation (2.13) for a continuous time varying injection can be obtained as convolution of the kernel function γ_M and the release function $m(t)$ expressing the variation in time of the released mass. The kernel function is obtained by solving the Equation (2.13) with initial condition $\gamma_M(0, \tau^*) = 0$, while the boundary conditions are: $\gamma_M(T^*, 0) = \delta(T^*)$ (instantaneous injection of a unitary mass at $\tau^* = 0$) and $\lim_{\tau^* \to \infty} \gamma_M(T^*, \tau^*) = 0$ [103] (cf. eq. 11):

$$\gamma_M(T^*, \tau^*) = \frac{\tau^*}{\sqrt{\frac{4\pi T^{*3}}{Pe}}}\, exp\left[\frac{-Pe(T^* - \tau^*)^2}{4T^*}\right] \tag{2.14}$$

The global transfer function $f_M(T^*)$ is therefore obtained by averaging over all the travel times:

$$f_M(T^*) = \int_0^\infty \gamma_M(T^*, \tau^*) f_\tau(\tau^*) d\tau^* \tag{2.15}$$

where $f_\tau(\tau^*)$ is the dimensionless probability density function of the travel time in the stationary case.
The travel time pdf assumes the following expression [45]. The general dimension $[1/T]$ equation of $f_\tau(\tau)$ is the following:

$$f_\tau(\tau) = \left(\frac{\mu_\tau^3}{2\pi\sigma_\tau^2\tau^3}\right)^{1/2} exp\left(\frac{-\mu_\tau(\tau-\mu_\tau)^2}{2\sigma_\tau^2\tau}\right) \tag{2.16}$$

where $\mu_\tau[T]$ is the first order moment and $\sigma_\tau[T^2]$ is the second order moment. They assume the following expressions:

$$\mu^*{}_\tau = \frac{L}{L_0} \tag{2.17}$$

and

$$\sigma_\tau^{*2} = \frac{2\sigma_u^2}{< v_0^2 >} \frac{I_v L}{L_0^2} = \beta \mu^*{}_\tau \tag{2.18}$$

where σ_u^2 and I_v are the variance and the integral scale of the velocity field, the hydrological carrier of the solute, and $\beta = 2\sigma_u^2 I_v/(< v_0^2 > L_0)$ is a dimensionless parameter describing how the variance of travel time increases with the distance from the source. The distances L and L_0 assume different meaning depending on the hydrological system considered. For the case of a single channel $L_0 = L$ is the length of the channel, such that $\mu^*{}_\tau = 1$ and $\sigma_\tau^{*2} = \beta$. On the other hand, in a channel belonging to a network, L_0 may be set to the average length of of the channels and L is the length of the single channel. In case of a river channel network, the velocity v_0 can be obtained from the

following expression: $v_0 = cQ^f$, where Q is a representative water discharge at the catchment's outlet.
The transfer function for the transient case $g(t)$ can be derived as follows:

$$g(t) = \frac{f_M(T^*)}{t_a}\frac{dT}{dt} \tag{2.19}$$

The solution in terms of concentration can be expressed by the following equation:

$$C(t) = \frac{Q_M(t)}{Q(t)} \tag{2.20}$$

where $Q(t)$ is the streamflow and $Q_M(t)$ is the mass flux, which turns out to be:

$$Q_M(t) = \int_0^t m(t-t')g(t-t')dt' \tag{2.21}$$

Application and discussion of this mathematical framework will be perfomed at catchment scale and will be presented in a future paper.

Steady-state application for pharmaceuticals We model transport process of contaminants along the river network by means of the following one-dimensional Advection Dispersion Reaction Equation (ADRE) [17]:

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = D_L\frac{\partial^2 C}{\partial x^2} + R \tag{2.22}$$

where C $[M/L^3]$ is the solute concentration, x $[L]$ is the Lagrangian coordinate measured along the stream, t $[T]$ is time, v $[L/T]$ is the mean velocity, assumed constant along the stream,

D_L $[L^2/T]$ is the local dispersion coefficient and R $[-]$ is the sink/source term representing the chemical reactions. Equation (2.22) is applied to a single stream under the simplifying hypothesis that flow is stationary and that the velocity is constant. The Equation (2.22) is the same as Equation (2.1).
The solute decays according to a first-order irreversible reaction $R = -k\,C$, where k is the reaction rate. By introducing the following transformation $C(x,t) = \tilde{C}(x,t)e^{-k\,t}$, Equation (2.22) reduces to the classical Advection Dispersion Equation (ADE) in the transformed concentration $\tilde{C}$:

$$\frac{\partial \tilde{C}}{\partial t} + v\frac{\partial \tilde{C}}{\partial x} = D_L\frac{\partial^2 \tilde{C}}{\partial x^2} \tag{2.23}$$

The model is completed by suitable initial and boundary conditions. The initial condition is of zero concentration along the stream $C(x,0) = 0$. A suitable upstream boundary condition, mimicking the typical release conditions at the waste water treatment plants is of continuous mass injection $M(t)$ at the position x_0. In addition, we assume that the stream is indefinite with the boundary condition at $x \to \infty$ of zero mass flux. This condition is equivalent to assuming that the downstream boundary condition does not affect mass flux.
Owing to the linearity of the Equation (2.22) the mass flux Q_M of the solute at a given control section x along the stream assumes the following expression:

$$Q_M(x,t) = \int_0^t \dot{M}(t_0)\, g_M(x, t-t_0)\, d\,t_0 \tag{2.24}$$

where $\dot{M}$ is the rate at which the mass is released to the stream at the position $x = x_0$. In Equation (2.24) the transfer function assumes the following form:

$$g_M(x,t) = g(x,t)\, e^{-k\,t} \tag{2.25}$$

with g $[T^{-1}]$ representing the solution of the Equation (2.23) for an instantaneous injection of a unitary mass of solute:

$$\tilde{C}_F(x_0,t) = \frac{\delta(t-t_0)}{Q} \tag{2.26}$$

where $\tilde{C}_F = Q_M/Q$ $[M/L^3]$ is the flux concentration (i.e., the ratio between the mass flux Q_M and the water discharge Q) and $\delta(\cdot)$ $[T^{-1}]$ is the Dirac delta. Finally, g is the solution of the Equation (2.23) for an instantaneous injection of a unitary mass [103]:

$$g(x,t) = \frac{x-x_0}{\sqrt{4\pi\, D_L\, t^3}} \exp\left[-\frac{(x-x_0-v\,t)^2}{4\,D_L\,t}\right] \tag{2.27}$$

In the general case of more than one release point along the river network, and taking advantage of the linearity of the transport equation (2.23) the expression (2.24) can be generalized as follows:

$$\begin{aligned} Q_M(t) = \int_0^t C_0(t_0)\, Q_0(t_0)\, g_M(L_0, t-t_0)\, d\,t_0 + \\ \sum_{j=1}^{N} \int_0^t \gamma_j P_j(t_0) g_M(L_j, t-t_0)\, d\,t_0 \end{aligned} \tag{2.28}$$

where L_0 is the distance of the source from the control section. The position of the source corresponds to the section at which the main stem, along which the control section is located, enters into the area of interest. Similarly, L_j is the distance of the $j-$th releasing point from the control section and γ_j is the mass per unit time and person released at the $j-$th point along the

network (from now on it will be called as theoretical load coefficient) and $P_j(t)$ is the number of persons at time t contributing to the section j.

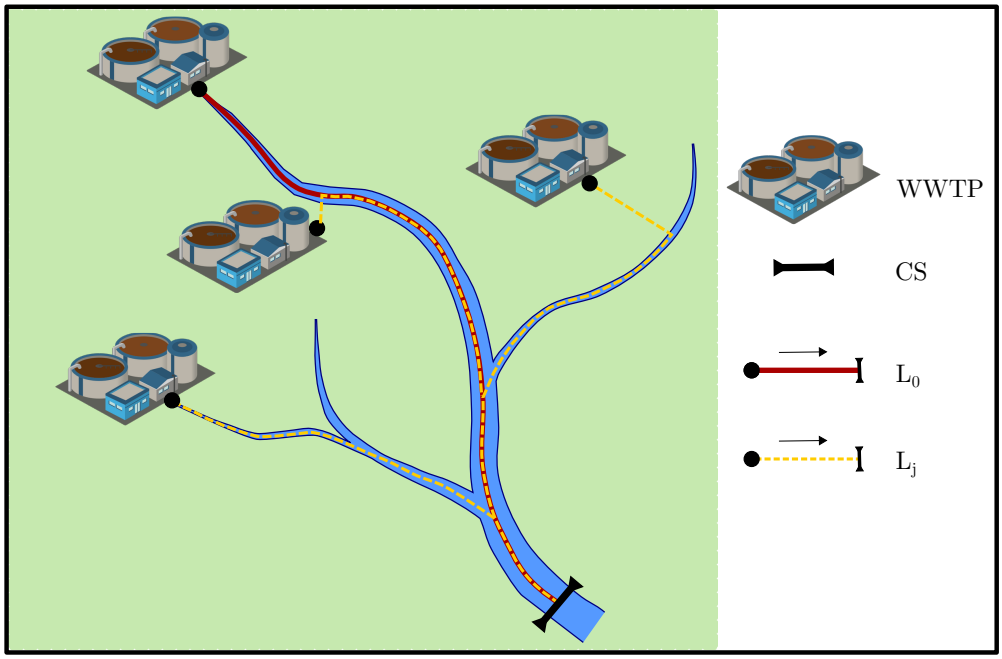

Figure 2.5: *Example of the model scheme: WWTPs that release contaminant to both the main stem and its tributaries are considered as point injections of pharmaceuticals. The distance between each WWTP and the river is calculated as the shortest orthogonal line between the two points. The distance between the release and the Control Section (CS) is defined as L_0 if the WWTP is located in the initial section of the basin whereas L_j if the WWTP belongs to tributaries of the main stem or if it is situated downstream the initial section.*

The mass per unit time and person can be expressed as follows:

$$\gamma_j = \frac{(\alpha D \beta)_j}{\Delta T} \tag{2.29}$$

where α [−] is the assimilation factor, corresponding to the fraction of dose D [M/day] that is released by the human body, β [−] is the percentage of usage of the targeted active principle and ΔT is the transformation factor of time to make the units congruent in Equation (2.24). Preliminary simulations

evidenced that dilution and decay effects overwhelm the dispersion effects (D_L). This is in line with the classical results of the study by [155], showing that geomorphological dispersion overwhelms local dispersion in shaping the hydrological response of a catchment. In the application discussed in Sec. 3.3.2 we assumed $D_L \to 0$, such that Equation (2.28), expressed in term of concentration and considering a discrete number of point injection, assumes the following form:

$$C_{m(i,j)}(t) = \left[C_0(t) Q_0 \exp\left(-k_i \frac{L_0}{v}\right) + \frac{\gamma_i}{\Delta T} \sum_{j=1}^{N} P_j(t) \exp\left(-k_i \frac{L_j}{v}\right) \right] \frac{1}{Q_m} \tag{2.30}$$

where $C_0(t)\, Q_0$ is the mass flux boundary condition which corresponds to the most upstream measuring point, L_0 and L_j are the distances defined in Equation (2.28) and γ_i and k_i are the two model parameters, specified for each i-th pharmaceutical. Both in calibration and application at catchment scale, velocity values were estimated as: $v(t) = cQ(t)^m$ assuming $c = 0.85$ and $m = 0.1$ [107]. The use of the previous consolidated experimental formula for the estimation of velocity data avoids the knowledge of the hydraulic section geometry, reducing input data requirements otherwise necessary in the two existing models (i.e., PhATE and GREAT-ER) [11, 60, 77].

CHAPTER 3

RESULTS

3.1 Driver detection of existing water quality trends in the Adige, Ebro and Sava river basins

3.1.1 Trends in drivers

Preliminary analyses of the selected drivers of water quality trends were performed in order to examine their temporal and spatial patterns in the study period (Figures 3.1 and 3.2). According to [116], the analysis of historical daily time series (1971 to 2010) indicated a severe decline in streamflow for the Ebro and downward patterns for the Sava, whereas no significant trends were detected in the Adige. MK-trend analysis of Q_m time series in the period 1990 – 2015 confirms the decline for the Ebro (Figure 3.1C) and the Sava (Figure 3.1E). However, apparently in contrast with the previous analysis of the daily data, the Adige also shows a predominance of negative trends in Q_m (Figure 3.1A), particularly in the Noce catchment. These differences may be due to the shorter observational period in addition to the fact that the gauging stations were not the same

used in the previous analysis. This suggests a more complex streamflow pattern in both space and time within the Adige catchment, with respect to the other two river basins. For what concern temperature, Adige and Ebro show large positive MK trends in TA (Figures 3.1B and 3.1D); this tendency is not confirmed in the Sava, where TA is nearly constant (Figure 3.1F).

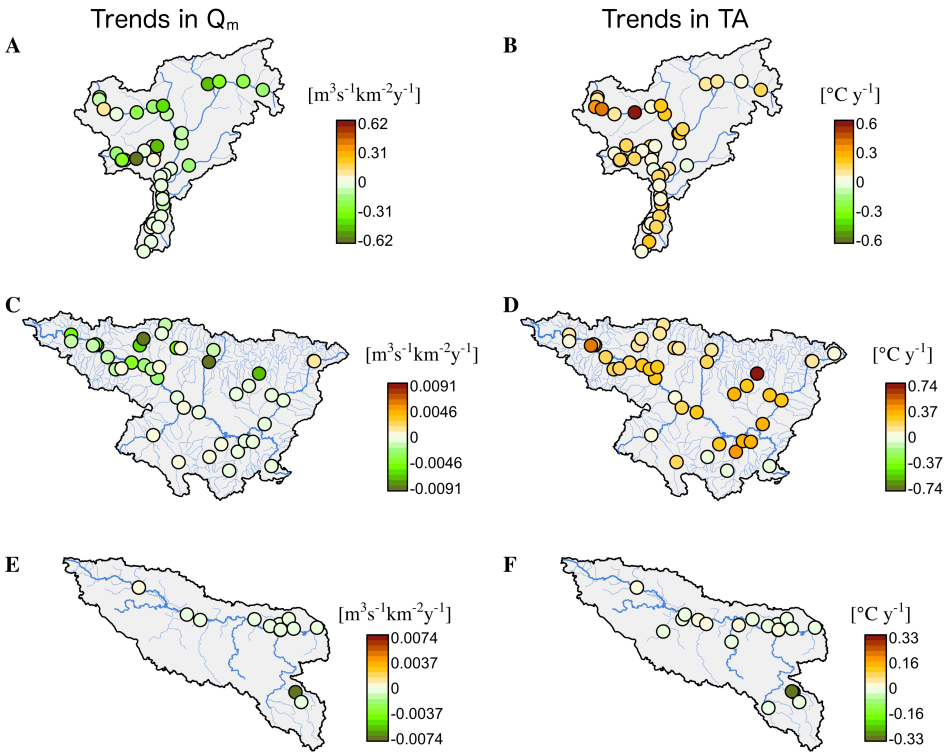

Figure 3.1: *Sen's slope trend magnitudes of monthly specific streamflow (left) and monthly air temperature (right) for Adige (A, B), Ebro (C, D) and Sava (E, F), respectively. Changes for both drivers refer to the period 1990-2015. In order to make the time series of the three basins comparable, streamflow time series were normalised by the drainage area at the sampling point.*

The percentage variations of agricultural land use and population density were derived for the three basins in the period 1990-2015. In the Adige, agricultural area decreased from 1990 to 2012 (-1.27%) while population increased (+17.81%). The reduction of agricultural area is more pronounced in the catchments of the tributaries Noce, Fersina and Avisio (Figure

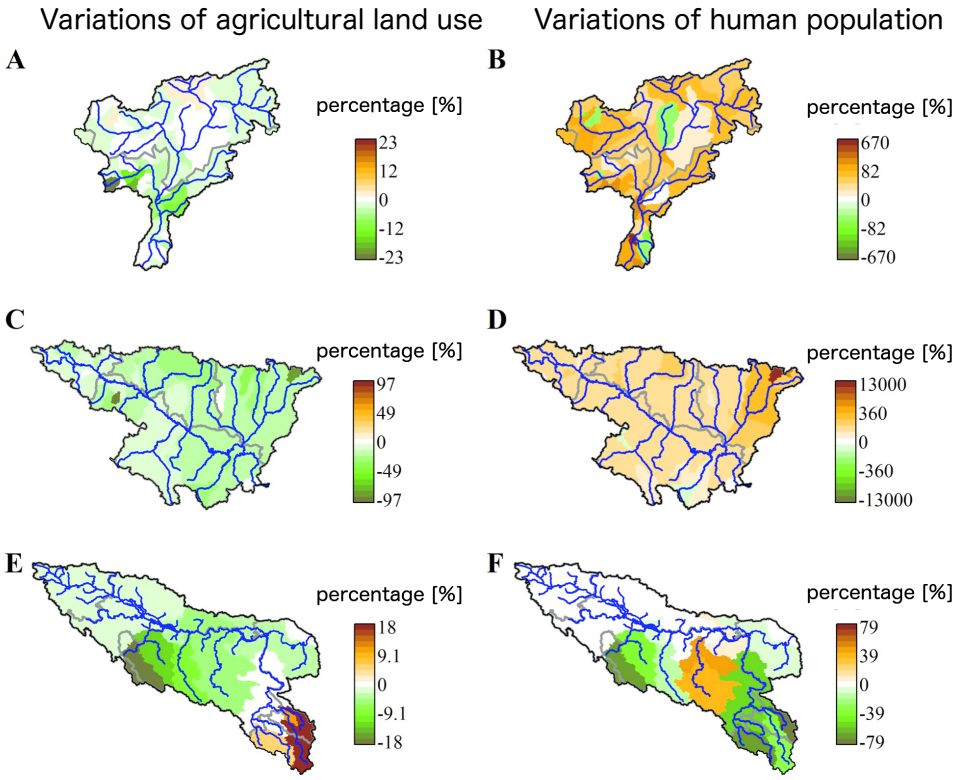

Figure 3.2: *Relative changes in the proportion of agricultural land use (left) and population per km^2 (right) aggregated over the sub-basins in the Adige (A, B), Ebro (C, D) and Sava (E, F). Changes in agricultural land use refer to the period 1990 to 2012 for the Adige (A) and Ebro (C), and to the period 2000 to 2012 for the Sava (E), respectively. Population changes are calculated for the period 1990 to 2015 in all basins.*

3.2A). Population increased over the majority of the sub-basins, with areas in the South and West showing the strongest population growth (Figure 3.2B). In the Ebro, agricultural area decreased in the period 1990-2012 (-9.68%), particularly from 2006 to 2012, whereas population increased by more than half (+53.12%) between 1990 and 2015. The reduction of agricultural land use is strongest in two headwaters in the western and north-eastern portions of the basin, respectively (Figure 3.2C). The latter region also shows the largest population growth. Population has reduced only in two headwaters of the southern Mediterranean region (Figure 3.2D). In the Sava, agricultural

area decreased slightly between 1990 and 2012 (-3.08%), while population remained fairly stable between 1990 and 2015. At the regional scale, agricultural land use shows a slightly to moderately reduction in all sub-basins except in the south-eastern region (Figure 3.2E). Regarding population, the upper and middle sections of the main river have experienced little change; in particular the Drina sub-basin (i.e., the south-eastern region) shows a decreasing tendency similar to the middle section South of the Sava River, and the Bosna sub-basin (between the latter two areas) shows increasing population (Figure 3.2F).

3.1.2 Correlation analysis

The statistical methods described in Sec. 2.3.1 were applied to the physico-chemical parameters and drivers. The Spearman's R rank correlation applied to the water quality indicators and drivers (Figure 3.3) helps in selecting among the 13 physico-chemical variables those that better represent the geochemical behaviour of the catchment for the following comparison with the drivers of change. Spearman's R rank coefficients indicate that the Adige basin has, in general, the highest mean correlations between the largest numbers of variables compared to Ebro and Sava. Electrical conductivity (cond), SO4, Cl and DO are negatively correlated with TA, while SS and TW are positively correlated with Q and Q_m. Differences are observed in the behaviour of physico-chemical variables in the three river basins. For example, both in Ebro and Sava, concentrations of Cl and SO4,electrical conductivity, and TW show positive correlations with TA, and all are negatively correlated with streamflow. On the other hand, similarities amongst the three basins emerge when considering negatively correlated pairs such as DO versus TA and TW and Q_m versus Cl.

Similarly, positive correlations are observed in all basins between TW and TA, which is expected being air temperature an important determinant for water temperature. As expected, Q and Q_m show a similar degree of correlation with geochemical variables, with Q_m showing a slightly larger correlation compared to Q. On the contrary, agricultural land use and population are weakly correlated with geochemical variables. In particular, the Adige dataset shows the lowest correlations: only population shows a negative correlation with BOD5, Ntot, PO_4, and P_tot. The highest correlation with these drivers is observed in the Ebro for As concentration. Furthermore, moderate mean positive correlations between agriculture and Ntot, and between agriculture and PO_4, respectively, are observed in the Ebro and Sava.

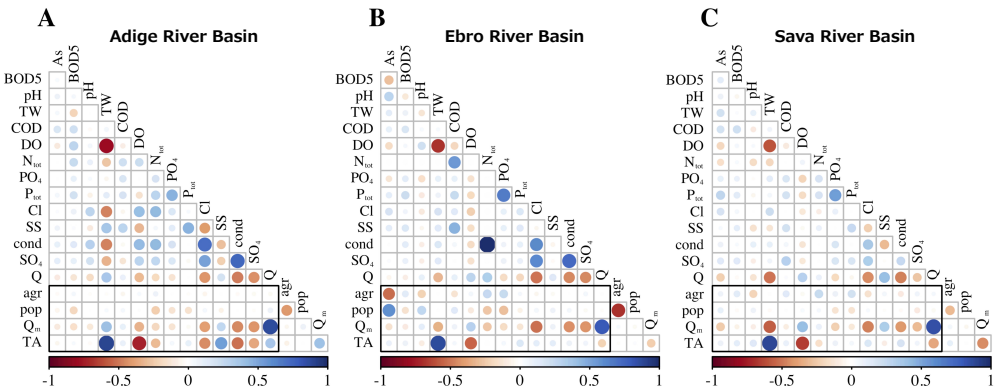

Figure 3.3: *Matrices of mean Spearman correlation between variables and drivers (black rectangles) for Adige (A), Ebro (B) and Sava (C) river basins obtained by averaging the correlation coefficients identified for each sampling location; red and blue dots correspond to negative and positive correlations, respectively. Small dots with light colour intensity represent low correlations while big dots with darker colours correspond to higher correlations. The rows in the correlation matrices referring to the drivers, which are agricultural land use (agr), population (pop), monthly mean water discharge (Q_m) and monthly mean temperature (TA), are included in a rectangular box.*

Spatio-temporal variations in driver-variable correlations might be masked because correlation coefficients at the sampling locations were averaged over the basin. To remove possible masking effects, PCA was performed. PCA is a robust technique for correlation analysis, which is not influenced by masking effects and eliminates accidental correlation (Figure 3.4). The basin with the highest variance explained by the first two principal components is the Sava (46.6%), followed by Adige (45.6%) and Ebro (41.9%). The results for the Adige basin (Figure 3.4A) confirm what was expected from geological characteristics; in the northern portion of the Adige (stations 104, 106, 107,109, 136), arsenic and sulphates are geogenic, since they are not correlated with anthropic factors such as agricultural land use and population. In the middle of the river basin (stations 115, 117, 212), at station SG000002 (Trento-Adige River) and at station 308 (Rienza River), anthropogenic influences are predominant: Cl, Ntot, pH are in fact correlated with agricultural land use and population. Moreover, PO_4 is highly correlated with streamflow. TA influences mostly stations 114, 265, 205 and shows positive correlations with TW, P_tot, BOD5 and SS, while it is negatively correlated with electrical conductivity and DO. In the Ebro basin, stations 101, 106, 18, 96, 97, 36, 3 are not influenced by any of the four drivers; however, pH and DO are the predominant variables for these sites: in fact, the respective arrows in Figure 6B are oriented toward the projected observations of these stations. Conversely, stations 11 and 20 are much more influenced by anthropogenic factors such as agricultural land use and population; both are highly correlated with SS and less with streamflow. Electrical conductivity, Cl, PO_4, COD and BOD5 show high positive correlations with agricultural land use and they are predominant at the sites 60, 33, 38 and 74. Finally, TA is highly correlated with TW and As, the correlation is

positive, and it influences stations 14, 15, 99 and 25. As opposed to the Adige, where stations can be divided into two groups according to PCA results, no clear drivers can be identified for the Ebro and the data do not show clustering effects.

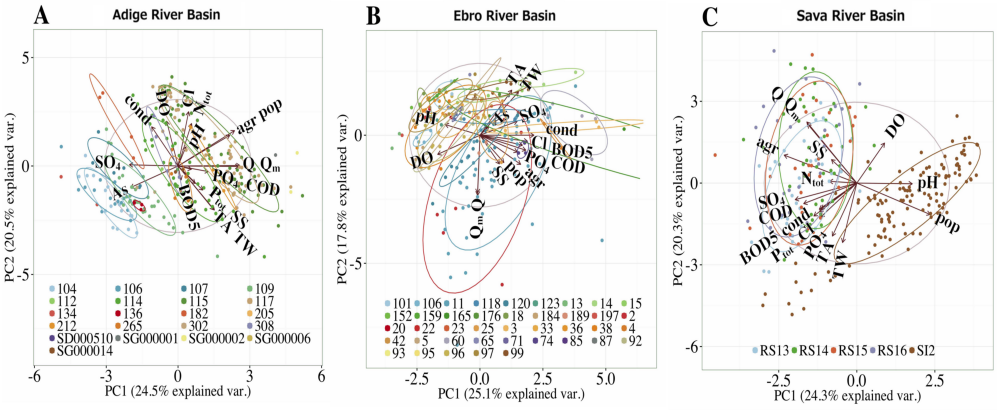

Figure 3.4: *Biplot representation of Principal Component Analysis between all time series of Adige (A), Ebro (B) and Sava (C), respectively. Points represent observations projected in the new reference system (PC1-PC2) and a different colour is assigned to each sampling site. Ellipses represent normal data probability with a confidence interval of 68%. Arrows represent variables whose reliability, in terms of variance, in the dataset is explained by their length; the angle between two arrows corresponds to their mutual correlation: 90° represents absence of correlation, whereas angles less than 90° indicate increasing positive correlation, and angles larger than 90° indicate increasing negative correlation.*

Finally, in the Sava basin, most of the sampling sites are highly influenced by agriculture: agricultural land use shows large correlations with SS and Ntot (Figure 3.4C). The only sampling site with a marked different behaviour is SI2, where population is the most influential factor: in fact, the variable has a strong positive correlation with pH and, differently from the other sites, SI2 seems to be much more affected by anthropic activities. In general, the analyses of the three basins confirm that DO is negatively correlated with TA whereas water and air temperature are highly correlated. These are expected results given that in surface waters air temperature is the main controlling factor of

water temperature and oxygen saturation in water depends on the water temperature.

3.1.3 Mann-Kendall trend test

In the following, we consider only parameters showing the highest correlations with drivers and describe the type of anthropogenic impact associated with the driver according to previous research. Based on these criteria, BOD5 and PO_4 were further analysed because of their correlation with agricultural practises [134]. Cl and electrical conductivity were considered because of their correlation with anthropogenic activities (e.g., contaminant releases from urban areas and mines), and industrial activities [76]. Electrical conductivity is also associated with variations in dissolved solids originating from land run-off [37]. In addition, DO concentration was selected as a primary physico-chemical variable for supporting interpretation of biological data given its importance for the aquatic life [96]. In fact, various aquatic species are particularly sensitive to changes of DO (see e.g.,[24, 34, 162, 164]). TW was selected because it influences the degradation of organic substances and is strongly correlated with TA, thereby encapsulating one of the most important effects of climate change in the riverine ecosystem [70]. Moreover, hereafter, we consider as driver only Q_m and no longer Q, as these two factors show very similar correlations with the drivers (see Figure 3.3 and Figure 3.4). Trend detection is influenced by the length of the time series, because cyclic variations at scales larger than the time window are seen as a trend [89]. To evaluate how large scale variations change with time, trend analysis was performed by using a moving time window of 10 years spanning the entire 1990-2015 time frame for six selected physico-chemical parameters (Figure 3.5). Notice that oscillating trends obtained

with a moving window of 10 years is indicative of variability with time scales of the order of 10 years, or less, while persistent trends are indicative of larger scales of variability.

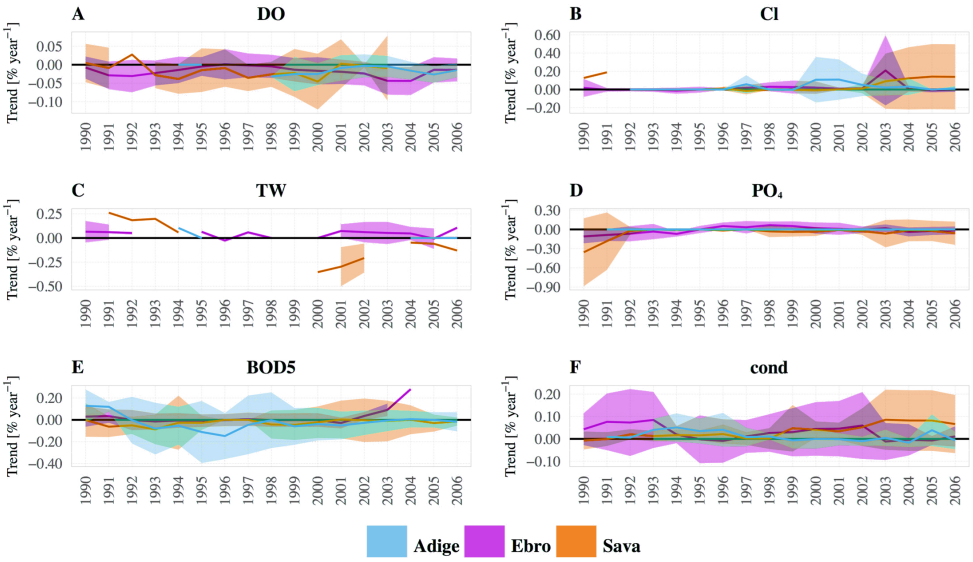

Figure 3.5: *MK mean trends (expressed as annual percentages of variation with respect to mean concentrations) on a moving time window of 10 years in the period 1990-2015 for the 6 water quality variables averaged over all the water quality stations of each basin. The abscissa shows the initial time of the 10 years window; therefore, the trend associated to the year 1990 is computed over the time window 1990-1999, and the trends for the following years up to 2006 are determined accordingly. Thick lines represent the mean trend whereas light colours indicate uncertainty bands expressed by standard deviation.*

DO shows a general negative trend with a small temporal variability in all decades and all basins: in both Adige and Ebro the majority of the stations show a downward trend, which intensified in the last decades (Figure 3.5A). Cl, PO_4 and BOD5 (Figure 3.5B, 3.5D, and 3.5E) show oscillating behaviours in the $'90_s$, but a stable, yet small, trend in more recent years. Both Cl and BOD5 show increasing trends for Ebro in the same decades (2002-2011, 2003-2012 and 2004-2013). Electrical conductivity does not show significant trends in the Adige, whereas it oscillates in the Sava and, in particular, in the Ebro basin (Figure

3.5F). The only basin showing increasing trends in electrical conductivity since 2003 on is the Sava. TW is the variable with the lowest variability, with a limited number of stations showing significant MK trends (Figure 3.5C). However, present trends indicate an increase of TW in the Ebro and a reduction in the Sava, particularly in the decade 2006-2015. Significant MK trends of a water quality parameter at a given station were associated with the drivers by using the Spearman rank correlation (Figure 3.6). TW is the only variable with positive trends in all the basins, though in the Adige and Sava this trend is significant only at a few stations. PO_4 trends are all positive in the Adige (Figure 3.6A) and related to three out of four drivers, while in the Ebro and Sava the simultaneous presence of both positive and negative trends is observed. Moreover, Sava (Figure 3.6C) shows the largest percentage of positive trends for Cl and BOD5, while Ebro presents the largest percentage of negative trends for DO. In the Adige, TA is the main driver of change for DO. Positive and negative trends are balanced with the latter dominating the north-western portion of the basin (Figure 3.6A). Cl concentrations show positive trends controlled predominantly by population in the north-western portion and by both population and the hydrological driver (Q_m) along the main stem after the confluence of the Isarco river (see Figure 3.6A). Positive trends in PO_4 and BOD5 are instead associated with population, though at a few stations it is the hydrological driver that exerts the main influence on the trend. Electrical conductivity and TW show significant trends in a small percentage of stations without a dominant driver. Note that in the north-eastern portion of the basin only a very limited number of monitoring stations show trends in the water quality variables. In the Ebro, trends of DO are predominantly negative and associated with TA, though at some stations the negative

trend is associated with streamflow, which is also the main driver of change for chloride and electrical conductivity. Agricultural land use is the main driver of change for BOD5, and population for PO_4. Overall, trends are predominantly negative for DO and positive for PO_4 and electrical conductivity, whereas for the other parameters positive and negative trends are balanced and without evident spatial patterns (see Figure 3.6B). In the Sava, less significant trends are observed, but they are still appreciable. Chloride is correlated with all the drivers except population, showing predominantly negative trends and no evident spatial patterns (Figure 3.6C). PO_4, BOD5 and electrical conductivity show positive trends correlated with agricultural land use, with BOD5 related to population. Finally, TW shows a single positive trend associated with the hydrological driver.

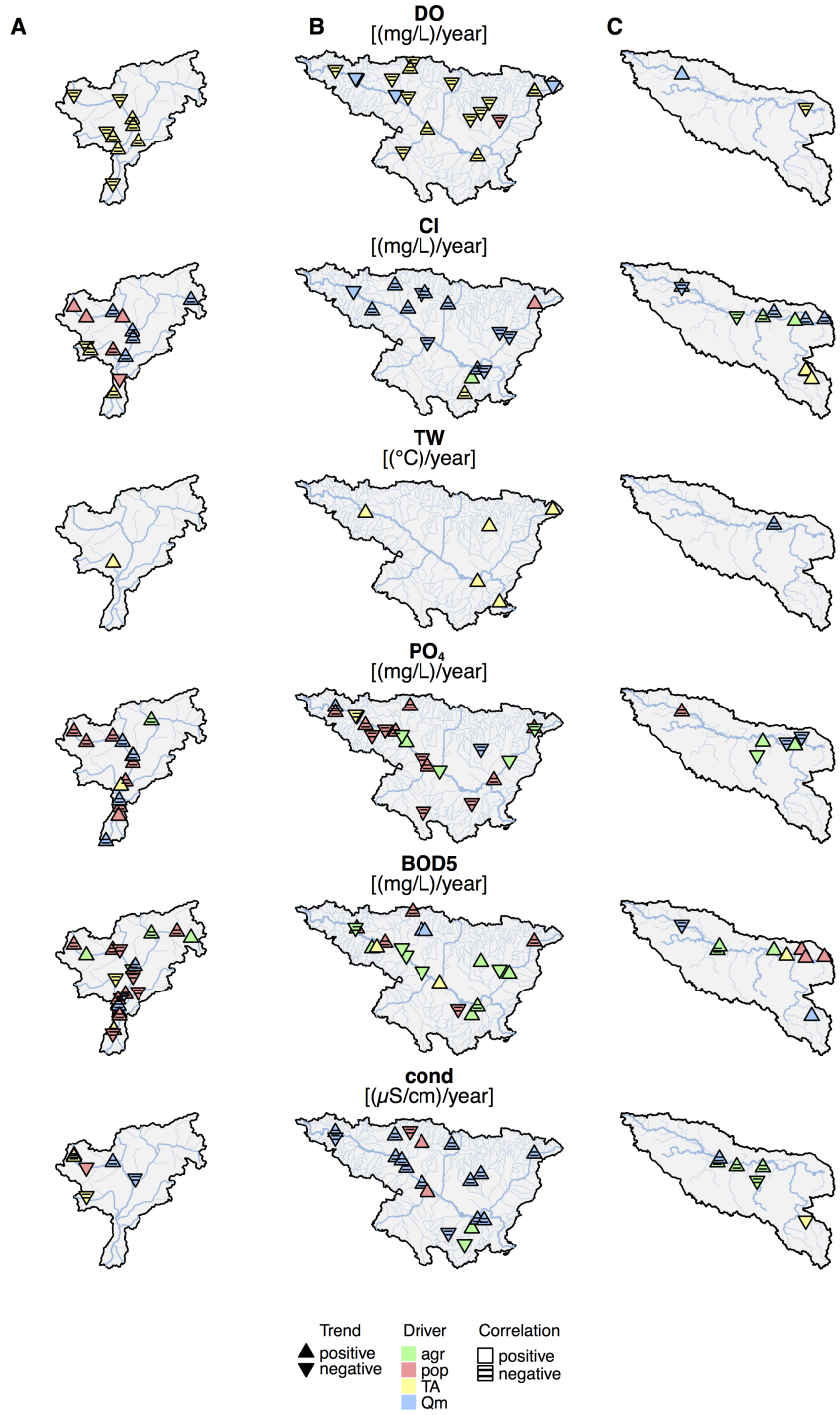

Figure 3.6: *Significant MK trends over the period 1990-2015 for the stations of Adige (A), Ebro (B) and Sava (C) river basins, respectively. Direction of triangles expresses the Sen's slope trend sign, whereas colours represent the driver with the maximum absolute value of Spearman correlation with the water quality parameter. Lines inside each triangle indicate a negative correlation between variables and the respective drivers; the absence of lines indicates positive correlations.*

DO is one of the most commonly used parameters for assessing ecosystem conditions, and it also influences solubility of potentially harmful metals [37]. It is inversely proportional to TW and hence TA, as confirmed in all the three basins by rank correlations (Figure 3.3), PCA (Figure 3.4) and trend analyses (Figures 3.5 and 3.6). The significant correlation of DO with TW was expected according to Henry's fundamental physical law [84] and thus it confirms that the dataset is of adequate quality to identify trends. Such correlation has beenwidely observed in the literature (see e.g., [38, 187]. In fact, Figures 3.1 and 3.6 show downward DO patterns in the northwestern part of the Adige River,which is associatedwith upward trends of TA (Figure 3.1B). Similar considerations are applicable to the northwestern part of the Ebro basin (Figure 3.1D) and to the eastern part of the Sava (Figure 3.1F). Even though TA is evidently the main driver of DO in all basins, DO concentrations were also observed to correlate with streamflow (Figure 3.6). In fact, DO concentrations are usually lower when streamflow is low (e.g. [18, 41, 193]: this is observed in the western part of Ebro and Sava basins (Figure 3.1C,ÄìE), but not in the Adige where DO correlates negatively with Q_m (Figure 3.3A). The latter evidence is probably due to the typical alpine hydrological regime of the Adige basin,with high streamflow occurring in summer. This suggests, in line with the findings of [41] for the Thames River and highlighted for the present study by Figures Figure 3.3 and Figure 3.6, that temperature is an important driver for DO even more than streamflow. In the Sava basin, DO trends are positive where streamflowincreases and negativewhere TA increases; however, according to this study, changes are relatively small. Another important factor affecting DO is the concentration of nutrients, which is provided both by nutrient-rich agriculture return flows [92] and by organic loads, the latter in the case of a concurrent

alteration of electrical conductivity [33, 48, 142]. In fact, nutrients promote biological activity, creating dead and decaying biomasswhich consumes DO as respiration [137, 138]. Moreover, the amplitudes of daily oxygen level variations were found to be strongly correlated with average nitrate concentration [187]. In the present study, though nutrients are not the primary drivers of DO changes, DO and phosphates are negatively correlated, especially in the Ebro and Sava basins, whereas the Adige basin is much less affected by nutrients (Figure 3.3). In addition, the Ebro and Sava basins are characterized by inverse correlations between DO and electrical conductivity, suggesting an influence of organic loads bywastewater on the observed DO decrease. Comparing the three basins, Ebro shows the greatest number of DO downward trends and, moreover, downward patterns are mostly associated with upward trends of TA. The combined effects of reduction of DO and streamflow [116], the latter being associated with reduction of precipitations and increase of TA, suggests that the Ebro is the basin with potentially the highest alterations of chemical and biological processes due to climate change [3, 27]. High chloride concentrations in surface waters may negatively impact aquatic life (Nielsen et al., 2003). Sources of chloride in surfacewaters are atmospheric deposition, weathering of sedimentary rocks, sewage and industrial effluents, agricultural and road run-off [37]. Dilution is crucial in limiting chloride concentrations in all the three basins, as chloride is negatively correlated with streamflow (Figure 3.3). As chloride concentrations in the Ebro are governed by the geology of the drainage area [27] , positive Cl trends in the Ebro basin are likely due to the reduction of streamflow (Figures 3.5 and 3.6B). An evident increasing trend in Cl concentrations is in fact observed in the north-western portion of the Ebro basin, where the

reduction of streamflow is pronounced (Figure 3.1C). A possible mechanism behind the increasing trend in Cl concentration is the increase of residence time, due to the reduction of streamflow, and therefore enhanced rock weathering, while the decrease of dilution due to streamflowreduction from areas not releasing Cl may have a synergetic effect. Similar behaviours are observed in the central area of the Adige and in the eastern portion of the Sava basin, albeit Cl is also correlated with population in the Adige and with agricultural land use in the Sava (Figure 3.6). In this context, population can be considered as a proxy of the impact of urban areas: in fact, municipal sewage treatment plants use chloride for removal of suspended particles and bacteria and to enhance the removal of phosphorus [159]. Nevertheless, road salt may also be a relevant source of these ions to surface waters, particularly in mountain catchments, where urban or industrial releases are expected to be of minor importance [159]. The combined analysis of Figures 3.2B and 3.6A leads to the conclusion that upward patterns of Cl in the north-western portion of the Adige basin and in the Noce sub-basin are linked to anthropogenic pressure. In the Sava, although analyses evidenced a predominant correlation with agriculture, the concurrent effect of anthropogenic emission of chloride has to be considered. In fact, the Sava River Basin is a very complex system influenced by industry, mining, treated and untreated wastewaters [55, 56, 80, 129]. Untreated urban wastewaters are of particular importance in Bosnia and Herzegovina and Serbia in the South-East of the basin, where less than 10% of agglomerations with person equivalent of more than 2,000 apply some kind of wastewater treatment. In addition, the major sources of surfacewater pollution in the southern part are industrial activities, farms and settlements which discharge untreated waters [147]. Moreover, the presence

of salt mines in Bosnia and Herzegovina [118] increased Cl concentrations in Bosna River, one of the main tributary of the Sava River. This is exacerbated by changes in the hydrogeological conditions, which enable the downward flow of freshwater causing additional salt dissolution [118]. Hence, the significant positive trends of Cl in the southern part of the Sava basin (Figure 3.6C) might be mainly related to industrial and mining activity [122]. TW does not show a clear pattern in all basins, which is due to the filtering effect (i.e., removal of stations presenting non-significant trends) of the Mann-Kendall test. Nevertheless, only positive trends are detected (Figure 3.6), which are linked to TA in Adige and Ebro, and to monthly streamflow in the Sava. This may evidence that climatic conditions (i.e., increasing TA) are impacting rivers by increasing TW. In fact, a larger TW leads to larger reaction rates of chemicals, which helps in degrading reactive contaminants, but at the same time causes alterations in the biogeochemical conditions [70]. Phosphorus is generally the limiting nutrient for algae growth [37]. Increases in phosphorus concentrations may be both of natural and anthropogenic origin: weathering of rocks containing phosphorus, decomposition of organic matter, fertiliser run-off and releases from domestic or industrial wastewater treatment plants (WWTPs) are the possible sources.Unlike previous variables, phosphate is less influenced by streamflow (Figure 3.6). Trends in the Adige basin are only positive in the period 1990-2015 and, according to our analyses, they aremainly correlated with population. This suggests that the principal source of phosphorus in the basin is anthropogenic, as also confirmed by [22]. Even though 80% P-removal at wastewater treatment plants outflows in rivers is required in Italy according to national law (D. Lgs n. 152, 11/05/99), an increase in population may have attenuated the

positive effects related to the implementation of this policy. Consequently, the increase of population in the southern and western areas of the basin (Figure 3.2B) may drive a further increase in phosphate concentrations. Unfortunately, information and studies on river nutrient loads, and in particular phosphates, are still incomplete for the Adige, as also suggested by [42]. Phosphate fertilisers and livestock data are available for the period 2002-2015, at annual scale and aggregated for the whole Trentino Alto Adige region, thus referring to an area larger than the Adige basin of about 3,000 km^2. These data did not show significant variations in the use of phosphate fertilisers, even if annual oscillations are quite pronounced (ranging from 8 to 65 kg km^2 in 2013 and 2014 respectively). Indeed, the number of adult bovine animals is slightly decreasing, with a peak of 20 units km^2 in 2012 and a minimum of about 12 units km^2 in 2014. These considerations reveal that increasing phosphate concentrations in the Adige basin can hardly be attributed to agriculture and livestock farming. Similar correlations are observed in the Ebro basin, where the positive trends in PO_4 correlate the most with population. This is consistent with [3, 180], who emphasize the important role of point sources, such as urban and industrial areas, in controlling phosphate concentration in rivers. In addition, livestock density increased in Spain, from a minimum of 17 units km^2 in 1990 to a maximum of 24 units km^2 in 2007. It is worth noting that these data refer to the entire state. However, downward patterns are also observed in some areas of the Ebro basin (Figures 3.5 and 3.6), possibly associated with the reduction in the use of fertilisers. Notice that in Spain the use of fertilisers declined from 1,200 to 700 kg km^2 in the period 2002-2014, as a positive effect of the introduction of drip irrigation [27] and improvements in sewage treatment [3]. Given

the overall downward trend in the proportion of agricultural land use (Figure 3.2C), the downward trend in the phosphate input from fertilisers might be counterbalanced, in the future, by the need to sustain the growth of specific and more water-use efficient productivity [73]. In the Sava, trends are on average upward but, in contrast to the Ebro, the largest number of positive trends is linked to agriculture. One possible source may be the use of P-containing fertilisers in rural areas of Croatia, Bosnia and Herzegovina and Serbia [129, 147], also according to the FAOSTAT (2015) data, which showed positive trends in the use of phosphate fertilisers in these three countries. Hence, our analysis identifies in agriculture a significant source of phosphate, supplementing and in some cases overcoming the release fromurban settlement, indicated as the main factor by [189]. This implies that phosphate concentrations might increase in the south-eastern region of the Sava, where agriculture expanded in recent years (Figure 3.2E). Moreover, livestock density increased across the basin, especially in Slovenia where it reached the highest values of the whole basin in 2011 with 103 units km^2 of cattle (FAOSTAT, 2015). Hence, this might also lead to increasing phosphate concentrations in the upstream section of the river basin. Nevertheless, the use of Pcontaining detergents released by municipal sewages and untreated waters might be important additional sources of phosphorus mainly in the northern part of the basin [129]. BOD5 is a measure of the amount of biochemically degradable organic matter contained in the water [37]: high concentrations of BOD5 in rivers produce, in general, oxygen depletion due to the decay of organic compounds [168]. The main sources of degradable organic matter are urban areas, but it may also originate from run-off of agricultural areas and cattle [62]. In all the three basins, we observed a prevalence of significant positive

trends in BOD5, whose sources are mainly urban for Adige and Sava and agricultural for the Ebro (Figure 3.6). Consequently, pollution with organic compounds may increase with population, particularly in the south of the Adige basin (Figure 3.2B), and in parts of the middle portion of the Sava basin (i.e., Bosnia and Herzegovina; Figure 3.2F), respectively. For the Adige basin, the introduction of the 70-90% BOD5-removal at WWTPs outflows (D. Lgs n. 152, 11/05/99) seems insufficient to counterbalance the increase of population. For the Ebro, in contrast, concentrations of organic compounds might decrease given the downward trend in the proportion of agricultural land use (Figure 3.2C). However, this might not apply to organic pollutants that are mainly discharged in industrial and municipal wastewater (e.g., alkylphenols; [177]). In general, BOD5 is expected to be inversely proportional to Q_m because of dilution [106]; however, both correlation and PCA analyses highlight a poor correlation between BOD5 and Q_m in all basins (Figures 3.3 and 3.4). BOD5 best correlates with agriculture and population but not with streamflow (Figure 3.6): this highlights the influence of anthropogenic activities on BOD5, as also confirmed by previous studies in the Adige [22], Ebro [27] and Sava [144]. Correlation between electrical conductivity and urban development is reported and such dependence has been attributed to the wash-off of solutes from hard surfaces in urban areas [37, 148]. In the Adige, electrical conductivity can be considered stable given the limited number of identified trends (both positive and negative). This contrasts with the Ebro and Sava, where significant and spatially coherent trends have been observed (Figure 3.6). In the Ebro, the predominance of positive trends ismainly associatedwith the reduction of streamflow; while in the Sava the positive trend is associated with agricultural activity (Figures 3.2E and 3.6), though a previous

work indicates an industrial source of electrical conductivity [55]. In addition, electrical conductivity is sensitive to variations in dissolved solids originating from land run-off [37]. However, it was not possible to analyse this factor in detail given the large-scale scope of this study.

3.2 Contamination sources and distribution patterns of pharmaceuticals and personal care products in the Adige River Basin

In the following, the analysis of the occurrence and spatial distribution of pharmaceuticals and personal care products (PPCPs; cf. Sec. 2.2.2) in the Adige River Basin is presented for the two seasons (i.e., winter and summer) when the sampling campaigns have been conducted. The average water discharges used for the following statistical analysis are presented in Table 3.1: hourly time series of instantaneous discharges for each sampling sites were averaged over the period of sampling both for winter and for summer seasons. The list of pharmaceuticals detected during both the sampling campaigns with the associated classes is presented in Table 3.2, whereas resident population and touristic fluxes specified for each sampling site and for both the two sampling campaigns are reported in Tables 3.3 and 3.4.

3.2.1 Occurrence and spatial distribution of selected PPCPs in winter

In general, 36 out of the 80 pharmaceutically active compounds (PhACs) investigated were detected in winter water samples with concentrations above the limits of quantifications (LOQ). The predominant pharmaceutical classes detected were the

Table 3.1: *Mean discharges for each sampling site and for both sampling campaigns: Q_{feb} are the average values of hourly water discharges in the period* 15/02-18/02*, whereas Q_{lug} are the average values of hourly water discharges in the period* 03/07-05/07

Sampling site	**Gauging station**	$\mathbf{Q}_{feb}$ **[m^3/s]**	$\mathbf{Q}_{lug}$ **[m^3/s]**
WB1	Tofflin Rio Barnes	0.340	0.810
WB2A-WB2B	Vermiglio	0.675	4.873
WB3A-WB3B	Pellizzano	2.342	16.909
WB4B	Ponte Moncovo	26.236	20.902
WB5B	Mezzolombardo	36.439	29.031
WB6B	San Michele	68.924	167.480
WB7A	Ponte S.Lorenzo	132.468	236.469
WB7B	Ponte S.Lorenzo	132.468	236.469
WB7C	Villa Lagarina	131.246	234.580
WB7D	Villa Lagarina	131.246	234.580

analgesics/anti-inflammatory and antihypertensives classes (see Figure 3.7).

Other pharmacological classes, in order of contribution, were antibiotics, diuretics and the psychiatric drugs. The analgesics/anti-inflammatories ibuprofen, diclofenac and salicylic acid were ubiquitous. The PhACs presenting the highest concentrations (> 300 ng L^{-1}) were diclofenac and valsartan, and the samples with the highest total pharmaceutical concentration in winter were at the sites WB2A and WB2B, located downstream of the Tonale WWTP (see Figure 2.3), which collect wastewater from a large ski resort. Moreover, in winter waters the total concentration of analgesics/anti-inflammatories was positively correlated with tourist arrivals ($r = 0.897$; $p < 0.05$). Regarding analgesics/anti-inflammatories pharmacological class, acetaminophen and naproxen were also often detected (92% of the samples), followed by codeine and ketoprofen with 75% positive detections. The highest total concentrations of analgesics/anti-inflammatory drugs were at

Table 3.2: *List of the pharmaceutically active compounds and the associated pharmaceutical classes detected in the Adige Basin samples.*

Classes	**Active substance**
Analgesics/anti-inflammatories	Codeine
	Piroxicam
	Indomethacine
	Ketoprofen
	Acetominophen
	Ibuprofen
	Salicylic acid
	Diclofenac
	Phenazone
	Naproxen
Lipid regulators and cholesterol lowering statin drugs	Bezafibrate
	Atrovastatin
	Gemfibrozil
Psychiatric drugs	Carbamezapine
	Lorazepam
	Citalopram
	Norfluoxetine
	Venlafaxine
β- Blocking agents	Propranolol
	Atenolol
	Sotalol
	Metoprolol
Diuretics	Hydrochlorothiazide
	Furosemide
Antihypertensives	Losartan
	Irbesartan
	Valsartan
Calcium channel blockers	Dilitiazem
	Verapamil
	Norverapamil
Antibiotics	Cefalexin
	Trimethoprim
	Metronidazole
	Erythromicin
	Sulfamethoxazole
	Clarithromycin
	Tetracycline
	Metronidazole

sites WB2A and WB2B (see Figure 3.7), with diclofenac concentration 675 ng L^{-1} at site 2B and 569 ng L^{-1} at site WB2A, respectively. Differences in concentrations between the individual sampling points were a result of increased river flow

Table 3.3: *Resident population and touristic fluxes reffered to each sampling site - winter sampling*

Sampling site	**Resident population**	**Touristic presences in hotels and** *B&B*	**Touristic presences in holiday homes**	**TOTAL**
WB1	252	0	0	252
WB2A-WB2B	1882	26655	1132	5679
WB3A	6289	7134	5624	19046
WB3B	7284	7814	6169	21266
WB4B	55008	12891	12126	80025
WB5B	57635	13663	12444	83742
WB6B	166164	17161	-	183325
WB7A	439166	69312	37700	546238
WB7B	463107	69312	37700	570119
WB7C	479872	72645	43113	595630
WB7D	486070	72645	43113	601828

and the consequent dilution effect. Acetaminophen, ketoprofen and ibuprofen had also increased concentrations at sites WB2A and WB2B (> 100 ng L^{-1}). In comparison with analgesics/anti-inflammatories, the total concentration of antihypertensive drugs in winter waters was positively and significantly correlated with the resident population ($r = 0.815$; $p < 0.05$). Amongst antihypertensive drugs, valsartan was the most abundant PhAC with detection frequency of 92%. The highest concentrations of valsartan occurred downstream the municipality of Trento (sites WB7A to WB7D) associated to WWTP Trento Sud (see Figure 2.3), with concentrations exceeding 300 ng L^{-1}. Increased concentrations of valsartan and other antihypertensive drugs were also detected at sites WB2A and WB2B (> 100 ng L^{-1}) but in lower concentrations than analgesics/anti-inflammatories. Amongst antibacterial drugs,

Table 3.4: *Resident population and touristic fluxes reffered to each sampling site - summer sampling*

Sampling site	**Resident population**	**Touristic presences in hotels and** *B&B*	**Touristic presences in holiday homes**	**TOTAL**
WB1	252	0	0	252
WB2A-WB2B	1882	561	238	2681
WB3A	6289	2084	1643	10016
WB3B	7284	2272	1793	11349
WB4B	55008	4622	4542	64172
WB5B	57635	5072	4734	67441
WB6B	166164	6428	-	172592
WB7A	439166	25934	14194	479294
WB7B	463107	25934	14194	503235
WB7C	479872	27236	16426	523534
WB7D	486070	27236	16426	529732

trimethoprim and sulfamethoxazole were the most frequently detected PhACs (detection frequency of 92%). The highest concentrations of trimethoprim, sulfamethoxazole, clarithromycin and metronidazole were also detected at sampling sites WB2A and WB2B (> 100 ng L^{-1}), while total concentration of antibiotics was positively and significantly correlated with the tourist arrivals ($r = 0.960$; $p < 0.05$). Finally, β-blocking agents were detected in concentrations < 70 ng L^{-1} and their total concentration was marginally correlated with the resident population ($r = 0.774$; $p < 0.1$). The high abundance of PhACs in sites WB2A and WB2B during winter sampling campaign may be explained by the increased number of tourist arrivals coupled with low flow conditions. In addition to pharmaceuticals, all analyzed samples contained between 1 and 10 different substances of personal care products (PCPs)

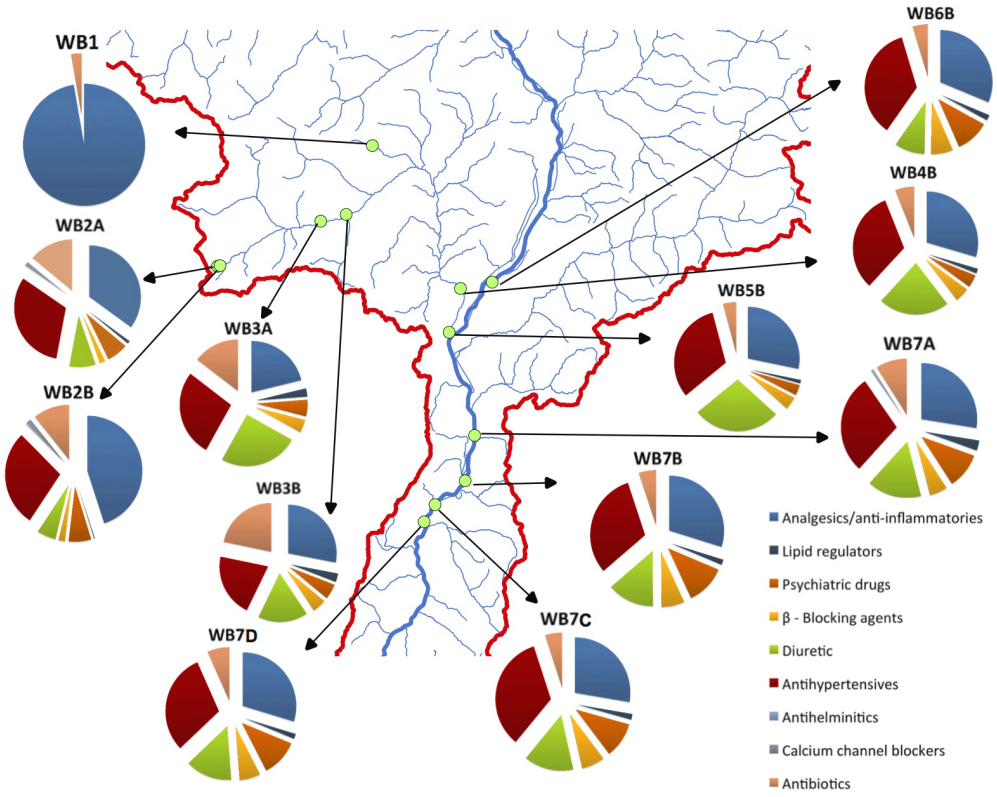

Figure 3.7: *Pie charts with percentages of pharmaceuticals concentrations detected in surficial waters during winter sampling campaign, associated to the sampling locations within the Adige River Basin. Pharmaceuticals were aggregated by class.*

residues. Overall, 13 out of the 25 investigated PCPs were detected with the concentrations above LOQ (Figure 3.8). Amongst them, the UV filter octyl-dimethyl-p-aminobenzoic acid (ODPABA) was ubiquitous. 4-Methyl-benzotriazole (4MeBZT) was also very frequently detected, in 92% of the samples, followed by the UV stabilizer 5, 6-dimethyl-1-H-benzotriazole (DMeBZT) and the paraben preservative ethyl paraben (EPB), both with 67% positive detections. Within the PCPs, the product with the maximum concentration was ODPABA (748 ng L^{-1} at site WB4B). Other two benzotriazole UV stabilizers (UV328 and UV329) showed concentrations of 669 and 553 ng L^{-1}, respectively, and were also frequently detected. Fragrances were seldom found (17%

frequency) and occurred at concentrations below 75 ng L^{-1} in the sites WB4B and WB2B. Another source of PCPs to sampling site WB4B is the nearby city of Trento.

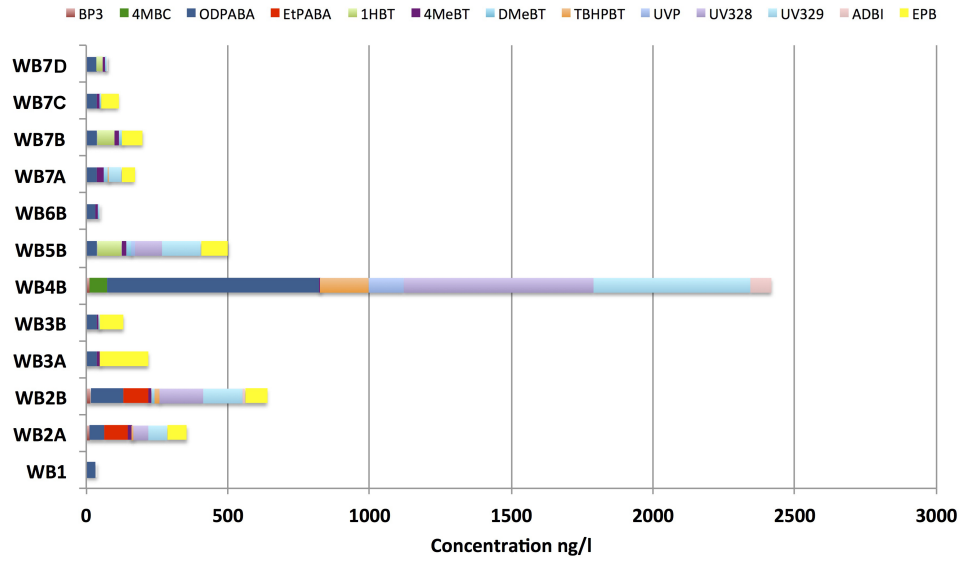

Figure 3.8: *Hystogram representing PCPs concentrations detected in surficial waters during winter campaign for each sampling site. Different colours corrispond to different PCPs.*

Concentrations and detection frequencies of PPCPs in winter were lower in sediments than in water samples. Only 7 pharmaceutical compounds were detected in the sediments with the concentrations above LOQ (see Figures 3.9 and 3.10). Amongst them, analgesics/anti-inflammatories were ubiquitous instead clarithromycin was detected in 83% of the samples, and trimethoprim in 58% of the samples. Clarithromycin was most common in sites WB2A and WB2B, (58.1 ng g^{-1} and 44.1 ng g^{-1}, respectively). Other PhACs were quantified with concentrations < 20 ng g^{-1}. Regarding PCPs, only three UV filters were detected in the winter samples of sediments with the concentrations above LOQ. Ethyl-p-aminobenzoic acid (Et-PABA, 67%), octocrylene (OC, 58%) and 3-(4'-methylbenzylidene) camphor (4MBC, 50%) showed concentrations below 8 ng g^{-1}/dw. The

total concentrations of camphors and PABA derivatives which are typically used in sunscreen lotions and other skincare products were significantly and positively correlated with the resident population ($r = 0.959$, $p < 0.05$; $r = 0.973, p < 0.05$). All sediments contained at least one UV filter, but OC was the compound measured at the highest concentration. In particular, the sediment sample collected at site WB7B showed the highest load of total PCPs, with a value of 8.30 ng g^{-1}/dw, being OCs more than a half of these. This UV filter is also a sunscreen agent that protects against UV-B and some UV-A rays.

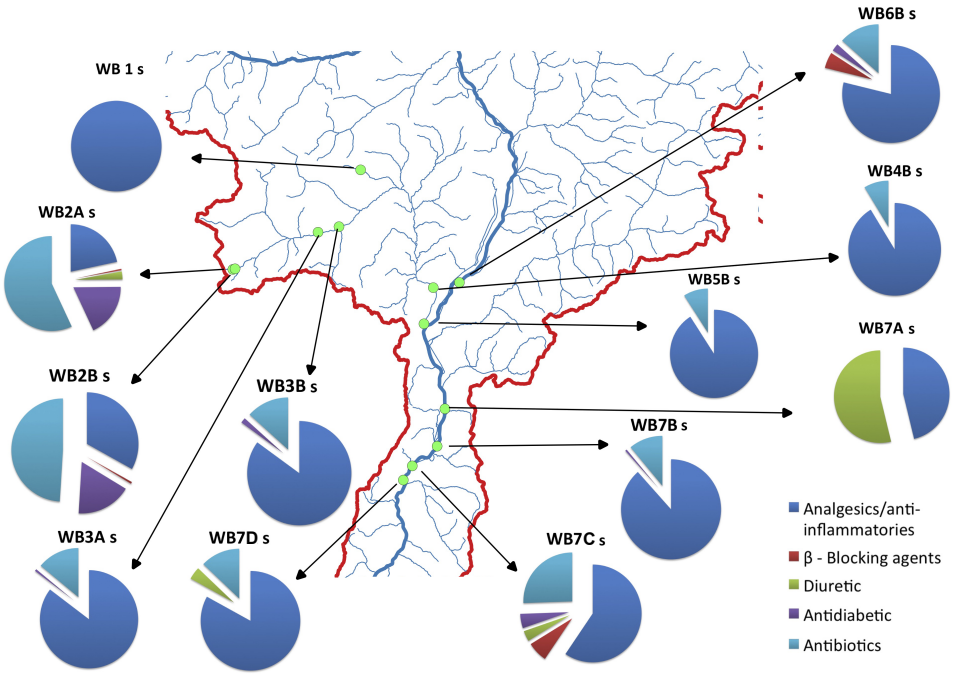

Figure 3.9: *Pie charts with percentages of pharmaceuticals concentrations detected in sediments during winter sampling campaign. Pharmaceuticals were aggregated by each family.*

3.2.2 Occurrence and spatial distribution of selected PPCPs in summer

In summer only 15 out of the 80 PhACs were detected with concentrations above LOQ, and usually in lower concentrations

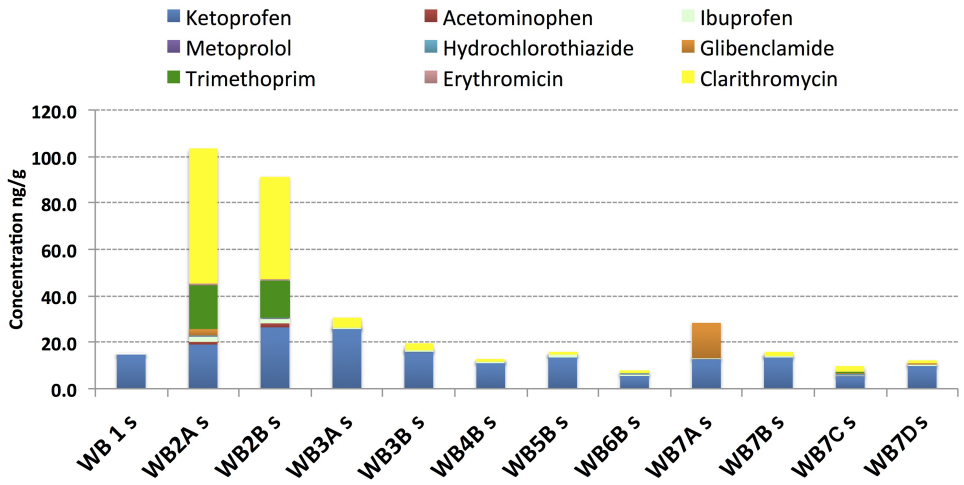

Figure 3.10: *Concentrations of pharmaceuticals detected in sediments during winter campaign, specified for each sampling point.*

than in winter (Figure 3.11). Most of the PhAC families were positively correlated during this period with the resident population ($p < 0.1$).

The analgesics/antiinflammatory salicylic acid was ubiquitous, while diuretic hydrochlorothiazide and the antihypertensive irbesartan were detected in the 92% of the samples. The predominant PhACs were analgesics/ anti-inflammatories (Figure 3.11), strongly and positively correlated with the resident population ($r = 0.887$; $p < 0.01$). Salicylic acid reached concentrations of 244 ng L^{-1} at site WB7B, and ketoprofen reached 67.1 ng L^{-1} at sampling site WB2B. Other analgesics/anti-inflammatory drugs were sporadically detected. Diuretics and antihypertensives were significantly correlated with the resident population ($p < 0.05$). Amongst diuretics, hydrochlorothiazide was the most abundant compound with concentrations up to 14.7 ng L^{-1} at the site WB7B. Irbesartan and valsartan were the most abundant antihypertensive drugs, though concentrationswere below 8 ng L^{-1}. Additionally, antibiotics were marginally correlated with the resident

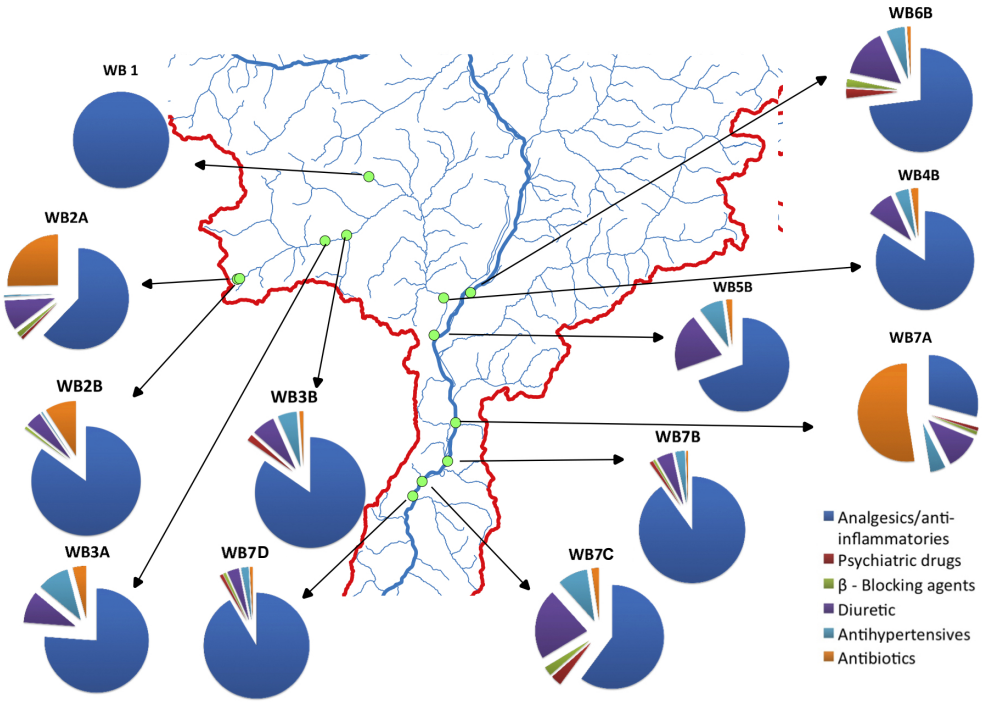

Figure 3.11: *Pie charts with percentages of pharmaceuticals concentrations detected in surficial waters during summer sampling campaign. Pharmaceuticals were aggregated by each class.*

population ($r = 0.872$; $p < 0.1$); with tetracycline being quantified up to 73.8 ng L^{-1} at sampling site WB7A. Other antibiotics were quantified at levels below 18 ng L^{-1}, respectively. Finally, psychiatric drugs were marginally correlated with the resident population and predominantly detected at sampling sites downstream of the city of Trento. Regarding PCPs, only 7 compounds were detected with the concentrations above LOQ and between 3 and 5 were simultaneously observed in the same sample. In summer waters, total concentrations of benzophenones and benzotriazoles were significantly and positively correlated ($p < 0.01$) with the resident population. The most polluted site was WB7D located downstream Trento. Benzophenone BP3 was ubiquitous,whereas the two benzotriazoles 1-H-benzotriazole (BZT) and MeBZT were present in 92% of the waters, mainly in

the lower part of the basin. In particular, BZT experienced a significant frequency and concentration increase. Similarly, BP3 was detected more often in summer than in winter and at higher concentrations (5720 ng L^{-1} at site WB7D), mostly in the lower part of the catchment (Figure 3.12).

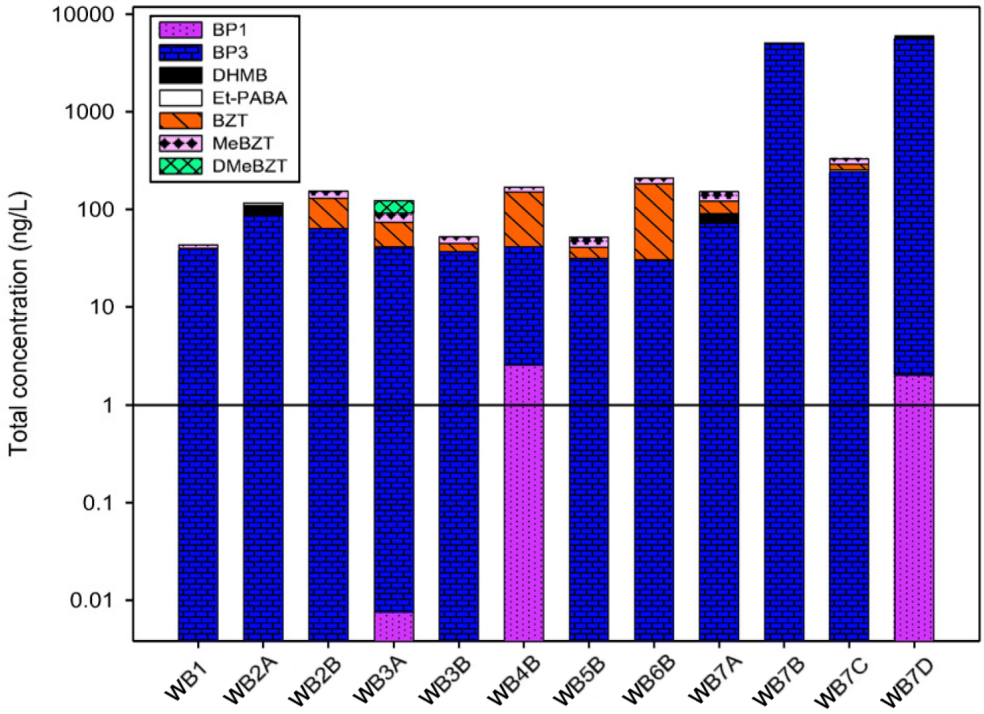

Figure 3.12: *Total concentrations of PCPs in water samples at all sampling locations: summer period. Notice the logarithmic scale of the ordinate.*

Besides, two of its metabolites benzophenone 1 (BP1) and 2, 2'-dihydroxy-4-methoxybenzophenone (DHMB) could be observed in 25% and 17% of the samples.
Very few PhACs were detected in the summer samples of sediments, usually at very low concentrations. The predominant PhACs were analgesics/ anti-inflammatories, which were ubiquitous and to follow antibiotics (Figure 3.13). The former class presented ketoprofen, ibuprofen and acetominophen whereas the latter in the detection of clarithromycin.

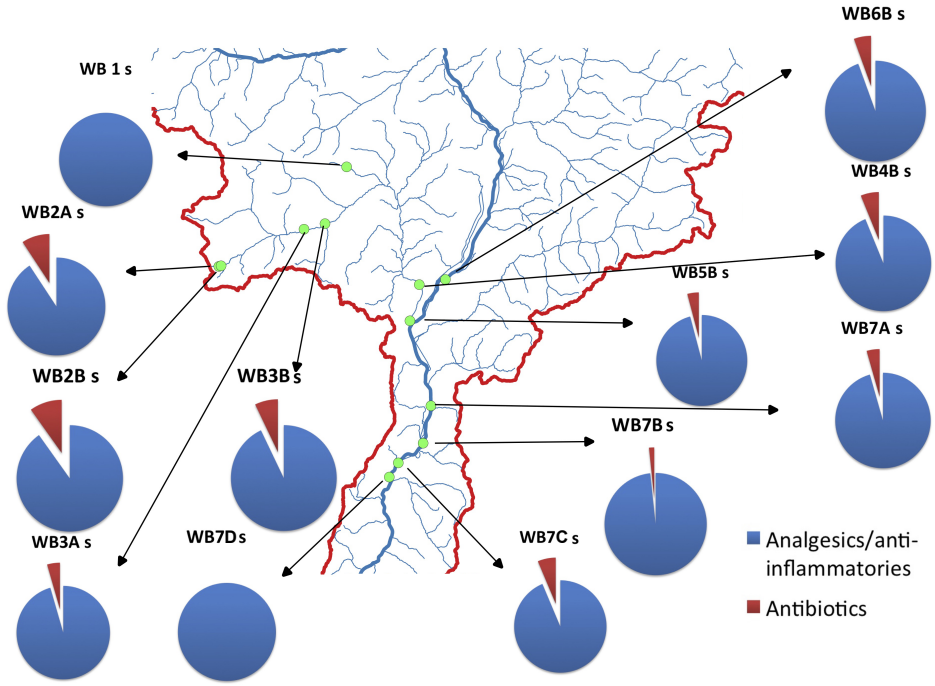

Figure 3.13: *Pie charts with percentages of pharmaceuticals concentrations detected in sediments during summer sampling campaign. Pharmaceuticals were aggregated by each class.*

In this period, the samples with the highest concentrations were collected at sites WB2A and WB2B, where clarithromycin was measured at 1.56 ng g^{-1} and 1.71 ng g^{-1}, respectively.

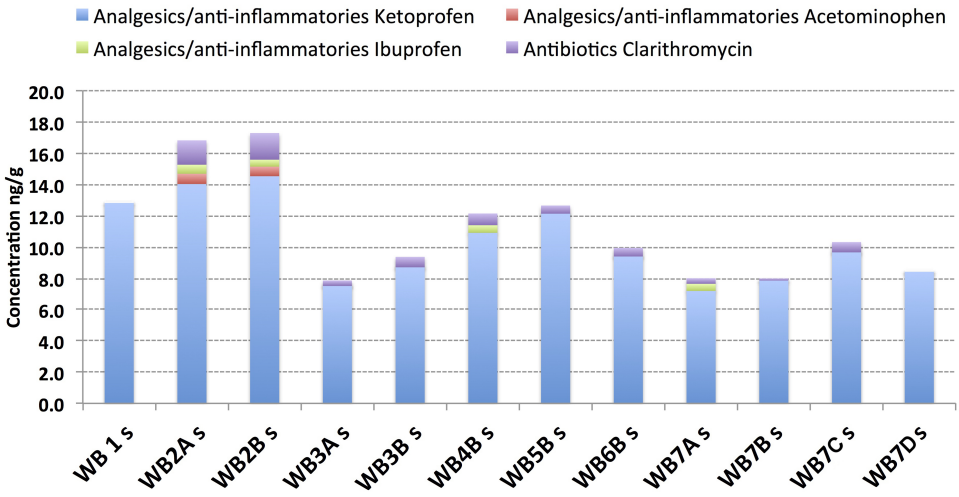

Figure 3.14: *Concentrations of pharmaceuticals detected in sediments during summer sampling campaign, specified for each site.*

Regarding PCPs in sediments, 4-hydroxybenzophenone (4HB) and OC were the most observed PCPs, which were found in 17% of the samples. Themaximumload of UV filters, 644 ng g^{-1}/dw was observed in WB2B sampling site and corresponded almost entirely to OC. This value is far above the maximum measured load in winter, 8.30 ng g^{-1}/dw.
In general, detected PPCPs concentrations during winter in the Adige were higher than in the summer period. This is mainly due to larger dilution from snow melting that occurs in summer, whereas in winter the predominance of solid precipitations produced low streamflow and thereby reduced dilution. The second important factor affecting PPCPs concentrations was tourism. Val di Sole, located upstream on the Noce River, is a district characterized by intense winter tourism arrivals. During February, tourist arrivals in Val di Sole accounted for 76.4% of the total population residing in the area, while this percentage was 9.7% in Valle dell'Adige and Vallagarina and 5.2% in Rotaliana. Therefore, the joint effect of low streamflow and a high number of tourists during winter produced ubiquitous higher concentrations of PPCPs, especially in the sites located within Val di Sole (WB2A/WB2B and WB3A/WB3B). On the contrary, PPCPs concentrations, which were detected in the downstream parts of the basin during winter, were mostly lower in comparison with the uppermost part, due to higher river flow in the lower part of the basin and to the lower number of tourist arrivals. Even though the PhACs consumption during winter is higher than in summer [143], high abundance of detected PhACs in Val di Sole could be additionally explained by the increased number of tourist arrivals (76.4% of the total population) during winter period. For certainty, analgesics/anti-inflammatories concentrations were associated to tourist arrivals during winter. In fact, ski resorts surrounding the Val di Sole produce

wastewater treated at the WWTPs of Tonale and Mezzana, and this could explain that the most abundant compound was an analgesic/anti-inflammatory (diclofenac). The non-steroidal anti-inflammatory (NSAID) diclofenac is a compound typically used in the treatment of sports injuries such as joint pain and inflammation [68]. This medicine works by reducing substances in the body that cause pain and inflammation and is mostly used in an oral form or as a topical cream. Amongst analgesics/anti-inflammatories, ketoprofen was another NSAID predominantly detected in the sampling sites WB2A and WB2B. Same as diclofenac, ketoprofen is also available as a gel, which can be applied directly to the skin to help relieve muscle and joint pain in sports injuries [51]. Analgesics/anti-inflammatories acetaminophen and naproxen were also detected with the highest concentrations in sampling sites WB2A and WB2B. Acetaminophen and naproxen are pain relievers and fever reducers [78]. In sampling sites WB2A and WB2B, the highest concentrations of the antibiotics trimethoprim, metronidazole, clarithromycin and sulfamethoxazole were detected. These antibiotics are usually used in order to treat certain bacterial infections, such as pneumonia, bronchitis, urinary tract infections and infections of the ears, sinuses, skin, and throat [110, 181]. It is common to observe these drugs during winter in order to treat cold-related illnesses [111]. Antihypertensive drugs were significantly correlated with the resident population, therefore pointing out urban centers as the main sources. The most abundant antihypertensive drug was valsartan and it was detected with the highest concentrations in the sites along the main stem of the Adige River, downstream the highly urbanized areas of the city of Trento. Valsartan is mainly used in the treatment of high blood pressure, heart failure, and in order to enhance the living chances after the heart attack [97]. Even

though touristic seasonal variations and streamflow are affecting PhACs occurrence, increased concentrations in winter waters can be also attributed to decreased operational conditions, configuration and performance of WWTPs during cold weather [91, 143, 163]. Higher concentrations and detection frequencies during low-flow conditions have also been reported [46, 101, 178]. Contrastingly, PCPs were not positively correlated with the tourist arrivals during winter. PCPs are not only incorporated in cosmetics but also occur in a wide range of products (plastics, adhesives, rubber, paint) [65, 150]. The most abundant PCP compound was ODPABA, particularly in the downstream sites (WB4B). Usually, ODPABA is added in conjunction with UV-A filters, being the most popular BP3. This compound is a powerful UV-B absorber, widely used in cosmetics as sunscreen [131]. Also EPB, a paraben occurred in winter. The parabens are a family of compounds extensively used as preservatives in the food, pharmaceutical, and personal care product industries, though their use is controversial for the potential carcinogenic and endocrine disruption properties [133]. The frequent detection of MeBZT and DMeBZT in winter waters may be associated with their wide use as UV absorbers in a variety of plastic products as well as anticorrosive agents, e.g., in aircraft deicer and anti-icer fluid (ADAF), and for so-called silver protection in dishwasher detergents. Due to their high water solubility, low biodegradability and limited sorption tendency, they are only partly removed in wastewater treatment [132]. Therefore, as a result of their extensive and varied use, benzotriazoles are often detected in river waters [10, 86]. Amongst the detected PPCPs, benzotriazoles, UV 328 and UV 329 were the most abundant compounds and both are efficient light stabilizers added to polyestyrene, poly (methyl methacrylate), polyester and ABS resins. Overall concentrations

of detected PPCPs were lower in the summer period. One of the most important factor influencing PPCPs concentrations during summer was higher dilution due to snow melting. Moreover, a general decrease in the consumption of PhACs in comparison with the winter period could account for these differences [143]. Even though the number of tourists increased in the lower area of the basin during this period, the percentage of tourists only increased the resident population of 4.8% in Valle dell'Adige and Vallagarina and 4.2% in Rotaliana. In addition, detected PPCPs concentrations during summer in the upstream sites were lower than in the downstream sites. This fact could be attributed to the combined effect of an increased stream flow and a significant decrease in the number of tourist arrivals in Val di Sole during summer months. The PhACs occurrence was associated with the population density in the area, while the profile of detected PhACs was also characteristic. Analgesics/anti-inflammatories, diuretics and antihypertensives were positively and significantly correlated with the resident population. In this period salicylic acid and the hydrochlorothiazide (used for hypertension, congestive heart failure, symptomatic edema, diabetes insipidus and renal tubular acidosis) [169] were the most frequent. Also, benzophenones and benzotriazoles were significantly and positively correlated with the resident population. The highest PCP load in summer was 6,000 ng L^{-1}, 2.5-folds higher than in winter (2417 ng L^{-1}). Therefore, considering the positive and significant correlation of PCPs with the resident population, the increase of PCPs during summer especially occurs at the sampling sites downstream the municipality of Trento. Additionally, high summer temperatures could also account for the general decreased PPCPs concentrations during summer, both because of the better elimination of PPCPs in WWTPs [46, 186], as well as by the decrease of human consumption and

increased natural degradation (photodegradation and biodegradation) [143]. The increased concentrations of PPCPs during winter and their decreased concentrations during summer were in accordance with the previous research in this field [143, 184, 186] and different performance studies of WWTPs during various seasons [105, 175]. Our measurements indicated that the accumulation of PPCPs in sediments was moderate in comparison to water samples. [128] reported that only the less polar pharmaceuticals may sorb to the deposit in sediments and suspended particles. Generally, compounds with basic characteristics (pKa > 7) showed higher tendency to bind to sediments such as clarithromycin (pKa 8.9), hydrochlorothiazide (pKa 7.9), metroprolol (pKa 14.1) and acetaminophen (pKa 9.38); which is expected, considering the rather polar property of the studied compounds and their low tendency to sorb to sediment [44]. The overall concentrations of PhACs in the winter samples of sediments were higher than those detected in the summer samples, possibly as a result of higher biodegradation during summer as a consequence of higher temperatures. The lower part of the catchment had the most contaminated sediments with PCPs, likely because of the accumulation of the transported materials along the basin. Also, the most abundant compound in sediments from both sampling campaigns was OC. Among the organic UV filters, OC is of particular concern due to its high lipophilicity (log Kow 6.88), stability, and resistance to photo-degradation. However, it can trigger the formation of potentially harmful ROS (reactive oxygen species) free radicals when it releases the absorbed energy. The widespread distribution of this sunscreen, along with the high concentrations determined in sewage sludge and sediments [66], appears to be correlated with its extensive use of beauty and hygiene products, especially, because both protects

in UVA and UVB regions, and improves the absorbing potential of other organic UV filters, such as BP3, EHMC, and avobenzone (AVB) [69]. Higher concentrations of OC occurred downstream the city of Trento. Our observed concentrations of PPCPs are in line with the ranges reported in literature [82, 150], whereas detected concentrations were typically in ngL^{-1}-μgL^{-1} level. Even though studies regarding spatiotemporal distribution of PPCPs are not frequent in the Alpine environments, our detected concentrations were comparable with studies performed by other authors [1, 14, 67, 98, 113]. The occurrence of PPCPs in fragile environments, like the Alpine aquatic ecosystems, represents an important threat due to their pseudo-persistency which can result in the acute effects on the environment and human health [29, 75]. Even though acute toxicity of PPCPs in the Adige River is unlikely to occur due to their usually very low environmental concentrations and to lack of chronic toxicity data regarding the effects of long-term and low-level exposures [16], seasonal touristic fluxes have shown to be a very important factor accounting for the overall PPCPs pollution of this Alpine ecosystem. To conclude, Alpine aquatic environments are extremely fragile systems to multiple stressors [31, 32, 192]. Combined and interacting influences of overexploitation, water pollution, flow modification, degradation of habitat and invasion by exotic species represent risks for global freshwater biodiversity and particularly for Alpine aquatic environments [57]. In the case of the Adige River, additional threats to the aquatic ecosystem include hydropeaking and thermopeaking due to hydropower production, climate change impacts, and emerging and regulated pollutants released by WWTPs [102].

3.3 Transport model of micro and emerging pollutants

The transport model for pharmaceuticals in rivers, presented in Sec. 2.3.2, has been tested to the Adige River Basin (cf. Sec. 2.1). In the following, the calibration procedure is described in Sec. 3.3.1, whereas the application to the whole Adige River Basin is presented in Sec. 3.3.2.

3.3.1 Inference of the model parameters

The concentration measures were used as observational data in the inference procedure that considered γ and k as the two model parameters (cf. Sec. 2.3.2). The inference procedure was performed in the Noce main stem since the size of this sub-basin (cf. Sec. 2.1) allowed introducing large amount of data maintaining good accuracy, and the subsequent application to the whole Adige River basin inherited the parameters obtained in the inversion with the Noce data in order to predict pharmaceutical concentrations in the Adige and its main tributaries, appreciating their temporal variations. The model encompasses all the implicit uncertainties associated with measurements, inter-annual population fluctuations, exact release points of the sewage effluents, and the parameters fluctuations. Streamflow data from all the existing gauging stations in the Noce sub-catchment were used for the calibration procedure. The sampling procedure for the values of the parameters considers the identification of a space of trial parameters, which were centered around a priori values of k and γ, respectively from available scientific literature and existing data on pharmaceutical market. In order to have a complete description of the parameter sampling space, the sampling procedure used is the well-known Latin Hypercube Sampling

(LHS)[124] with a log-normal prior distribution of the two parameters: the method generates controlled random samples extracted from each partitioned region of the parameter space, ensuring that all areas of the parameters space were sampled. The number of samples used was $N = 100$, whereas the number of runs was equal to $M = 10,000$. Owing both to the seasonality of parameters and to the different pharmaceuticals included, the two factors presented a high variability of even many different orders of magnitude. Moreover, parameters values must be, by definition, positive or at least equal to zero.
The optimality criteria adopted to select the parameters is the Maximum a Posteriori criteria (MAP), which is consistent with the hypothesis that the a priori distribution of the parameters is Multi-Normal or Multi-LogNormal [35, 125]:

$$L(a) = [z - \mathscr{F}(a)]^T C_v^{-1} [z - \mathscr{F}(a)] + \beta [\overline{a} - a]^T C_a^{-1} [\overline{a} - a] \quad (3.1)$$

where L is the objective function to minimize, a is the vector of the unknown model parameters, z is the vector containing the observational data, $\mathscr{F}$ represents the solution of Equation (2.30), C_v is diagonal matrix of the error variances and C_a is a diagonal matrix which epitomizes the effect of uncertainty associated with the prior information, $\overline{a}$ represents the prior estimates of the model's parameters and β is the constant controlling the weight of the regularization term with respect to the error term. In our simulations, we assumed $\beta = 1$. The optimal set of parameters is obtained by minimizing the Likelihood (Equation 3.1). Similarities in terms of the best set of parameters were also detected and tested by applying the well-known Nash-Sutcliffe Efficiency Index (NSE; [135]), which was used as a testing comparative method to evaluate the goodness of fit (i.e., difference between observed and simulated concentrations). The values of the parameters (i.e., γ and k) obtained through the

two methods and the goodness of fit between the observed and simulated concentrations are approximately the same, supporting and evidencing the assumptions of the Bayesian approach and the model applied.
Due to the seasonality of the two model parameters, γ and k may assume different values in the two sampling months (i.e., winter and summer campaigns). Moreover, considering the reduced number of measures, it may be appropriate to limit the number of model parameters as possible. For these reasons, we analyzed the accuracy of four different alternative models, introducing hypotheses on the seasonality of parameters and on the possibility to include them in the calibration procedure. Thus, including the two sampling campaigns in the calibration, the four possible models were evaluated and selected through the Akaike's information criterion (AIC; [5]) as the numerical expression that quantifies the amount of information and that determines statistically the number of parameters in an equation which represents a group of experimental data. In fact AIC shows that successive increase of the number of factors quickly lead to models that are not quite appropriate for the direct application of the method of maximum likelihood [6].

$$AIC = nlog\left(\frac{RSS}{n}\right) + 2k \tag{3.2}$$

where n is the number of experimental data points, RSS is the estimated residual of fitted model and k is the number of parameters.

The four models tested are the following:

1. absence of decay and a temporal constant theoretical load coefficient;
2. absence of decay and two values of the theoretical load coefficient, one for February samples and one for July;

3. two values of the constant of decay specified for the two sampling seasons and a temporal constant theoretical load coefficient;

4. two values for both the parameters specified for the two sampling seasons;

This last model, characterized by 4 parameters, embodies the seasonality in both the two factors and outwardly seems to include all possible uncertainties associated with parameters variations. Nevertheless, the application of the AIC to the previous models evidenced that this last case is over-parameterized, providing the highest values of AIC for all the pharmaceuticals. Comparable low values of AIC were obtained for the second and the third models (see previous enumeration): in order to include and estimate seasonality of the decay coefficient for the 5 selected pharmaceuticals, we selected the 3-parameter model with two values of k specified for the two sampling seasons (February and July) and a unique constant theoretical load coefficient, excluding its temporal variability. The concentrations simulated with the 3-parameter model with the Bayesian approach are presented in Figure 3.15. Diclofenac is the only pharmaceutical that represents an exception of the calibration procedure previously presented: in fact, its concentrations were detected only in February and hence, instead of a 3-parameter model, simulated concentrations were obtained through a 2-parameter model (i.e., considering only k for February and a unique theoretical load coefficient). Nevertheless, it shows the best fit with the lowest L-value (3.11; Figure 3.15 and Table 3.5). The simulated concentrations of all the other pharmaceuticals were calculated through the 3-parameter model. Among those, the compound with the lowest L value and hence the best goodness of fit is

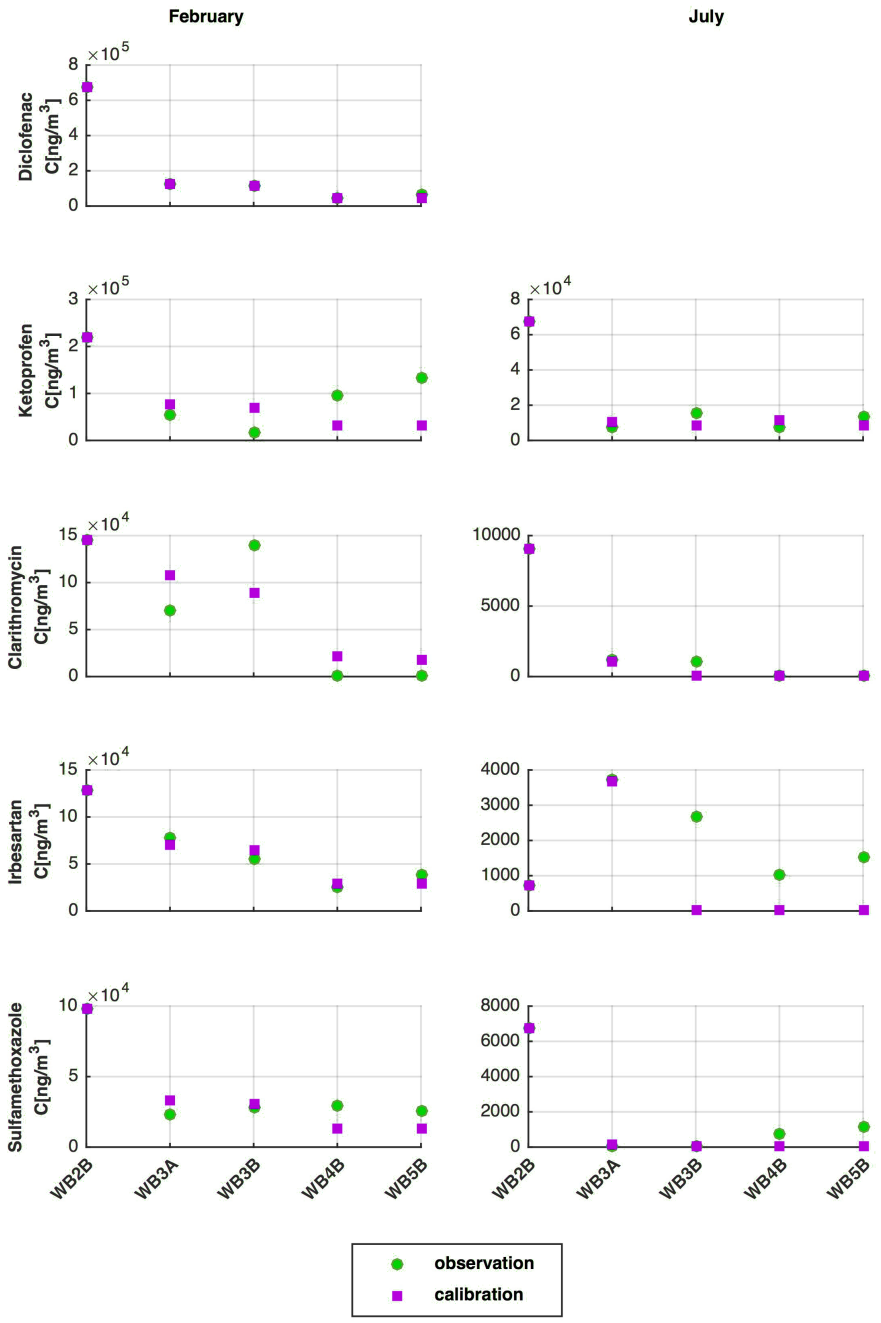

Figure 3.15: *Pharmaceutical concentrations of 5 selected compounds for both winter and summer campaigns. Purple points represents calibrated concentrations obtained through a three parameter model whereas green ones measured concentrations in the 5 selected points along Noce River. Diclofenac concentrations were detected only during winter campaign.*

clarithromycin (48.78; Table 3.5), whereas the pharmaceutical with the worst fit between simulated and observed concentrations is sulfamethoxazole with $L = 283.73$ (Table 3.5). More in detail, calibrated concentrations of sulfamethoxazole tend to underestimate in the last two sampling points of the Noce catchment (i.e., WB4B and WB5B) for both winter and summer campaigns while it tends to overestimate the measured values at point WB3A in winter (Figure 3.15). Instead for clarithromycin, the worst fit is detected for the winter campaign, characterized by an overestimation of the simulated concentrations in the sampling points WB3A, WB4B and WB5B and an underestimation in WB3B measuring site. Contrary to diclofenac, the other analgesic/anti-inflammatory selected in the present study (i.e., ketoprofen) evidences a better goodness of fit for the summer campaign than for the winter one with an underestimation in the last two measuring points (i.e., WB4B and WB5B). In general, ketoprofen displays similar objective function value than irbesartan: in fact, the former assumes the value of 60.45, whereas the latter is 71.77 (Table 3.5). The winter pattern of the simulated irbesartan follows almost perfectly the observed concentrations, whereas the same conclusion can not be achieved for the summer campaign where the discrepancy between the calibrated and observed concentrations is particularly evident in the last three sampling points. As expected, the calibrated values of the coefficients of decay are lower in winter than in summer: this is due to the temperature dependence of biological processes causing degradation. In fact, biodegradability is strongly dependent on environmental conditions among which it is worth citing water and air temperature. In general, among the five selected pharmaceuticals, diclofenac and ketoprofen are those less affected by decay during both winter and summer campaing,

while clarithromycin is the most affected compound during winter. Instead sulfamethoxazole is the pharmaceutical most influenced by decay thanks to the high value of the calibrated coeffient of decay (Table 3.5).

Table 3.5: *Theoretical load coefficients (γ) and coefficients of decay (κ) for the 5 pharmaceuticals.*

	First try		**Calibration**			
	γ	k	γ	$k_{february}$	k_{july}	**L**
Diclofenac	$2.09E+06$	$1.87E-05$	$2.03E+06$	$3.83E-09$	–	3.11
Ketoprofen	$1.19E+06$	$2.00E-05$	$1.30E+06$	$5.49E-09$	$4.60E-05$	60.45
Clarithromycin	$8.98E+06$	$3.25E-03$	$1.99E+06$	$2.77E-05$	$7.94E-03$	48.78
Irbesartan	$8.20E+05$	$8.53E-05$	$1.25E+06$	$4.29E-07$	$2.80E-03$	71.77
Sulfamethoxazole	$4.21E+05$	$4.42E-05$	$5.64E+05$	$1.58E-08$	$1.01E-02$	283.73

Figure 3.16 shows the matrices with the likelihood values obtained in the calibration procedure for the five selected pharmaceuticals and for both winter and summer campaigns. In

particular it shows the likelihood function L given by Equation (3.1) as a function of the parameters. To make the visualization clearer instead of using a three dimensional representation, L is represented in a two dimensional space as a function of γ and k. In general, Figure 3.16 shows a clear identifiability of the parameters for all the compounds, as shown by the dark blue area, representing small values of L, located away from the boundaries of the domain and of relatively small size. Among all the five studied contaminants, diclofenac shows the lowest L-values which are concentrated between $k_{february} = 7.1 \cdot e^{-11} - 1.1 \cdot e^{-6}$ and $\gamma = 1.5 \cdot e^{+6} - 2.3 \cdot e^{+6}$. Thus, ketoprofen presents a smaller interval for both winter and summer campaigns: in fact, $k_{february} = 5.8 \cdot e^{-11} - 5.8 \cdot e^{-7}$, $k_{july} \simeq 4.2 \cdot e^{-5}$ and $\gamma \simeq 1.1 \cdot e^{+6} - 1.3 \cdot e^{+6}$. Clarithomycin presents the lowest L-values in the intervals $k_{february} = 1.1 \cdot e^{-5} - 1.1 \cdot e^{-4}$, $k_{july} = 7.4 \cdot e^{-4} - 7.4 \cdot e^{-1}$ and $\gamma \simeq 2.0 \cdot e^{+6} - 2.2 \cdot e^{+6}$. Irbesartan shows the minimum between the intervals $k_{february} = 4.9 \cdot e^{-9} - 1.9 \cdot e^{-5}$, $k_{july} = 1.7 \cdot e^{-3} - 1.5 \cdot e^{-2}$ and $\gamma = 9 \cdot e^{+5} - 1.3 \cdot e^{+6}$ and sulfamethoxazole, the pharmaceuticals with the worst goodness of fit shows the minimum between the intervals $k_{february} = 9.9 \cdot e^{-9} - 3.9 \cdot e^{-6}$, $k_{july} = 8.8 \cdot e^{-4} - 2.6 \cdot e^{-2}$ and $\gamma \simeq 5 \cdot e^{+5}$. Considering the delimited area of the minimum values of the objective function, the model seems to represent and converge at the representative calibrated values of the three parameters. Moreover, as expected the optimal k values are smaller in winter than in summer and they are however rather small, suggesting that in the Alpine rivers dilution due to the increase of water discharge with the contributing area is the main attenuation mechanism for PPCPs reseased from WWTPs.

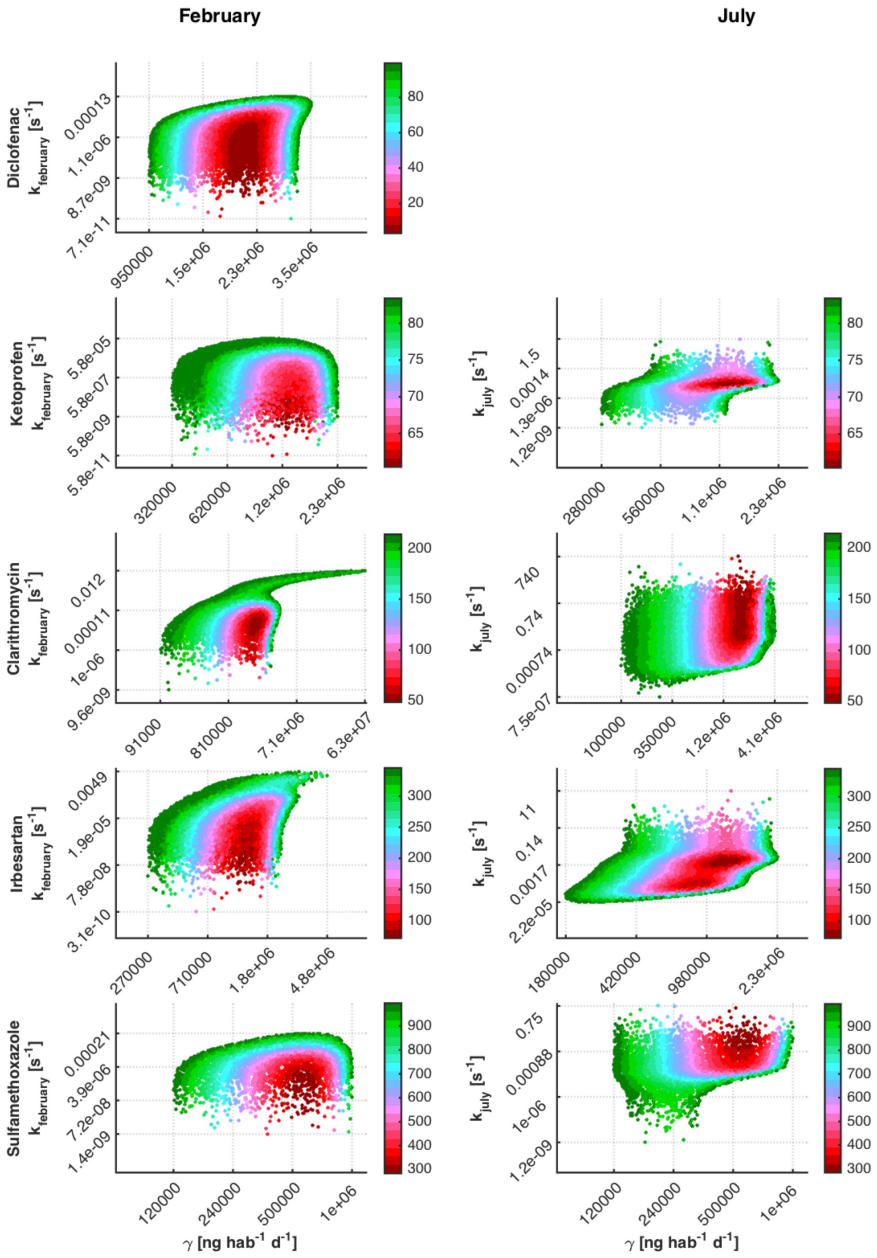

Figure 3.16: *Error matrices of the 5 selected pharmaceuticals for both winter and summer campaigns. Each dot represents the value of the objective function (L) for each pair of γ and k selected using the Latin Hypercube procedure. Green dots represent high values of L whereas red dots low L values. The best set of parameters is selected among the minimum of the red dots.*

3.3.2 Application at catchment scale

The model parameters obtained for each pharmaceutical through the calibration procedure were used for the definition of the chemical concentrations in the whole Adige River Basin limited to the year 2015. Some assumptions were made in order to apply the model: both parameters (γ and k) were assumed spatially constant for the basin. Moreover, including the seasonality of the coefficients of decay and its primary dependence on water temperature, k was assumed to vary according to the well-known Arrhenius law [13]).

$$k = Ae^{\frac{-E_A}{RT}} \tag{3.3}$$

where k is the coefficient of decay, A is the frequency factor, E_A is the activation energy, R is the gas constant and T is water temperature expressed in Kelvin. The terms A and E_A/R were calibrated for each pharmaceuticals by solving a system of two equations, the former with the winter data and the latter with summer ones. In order to solve the system for all pharmaceuticals, for diclofenac the value of the coefficient of decay for July was assumed equal to k_{july} of ketoprofen because they belong to the same pharmaceutical class. As input sources of contaminants, a selection of WWTPs was made, considering mainly WWTPs of the main towns and all the WWTPs with more than 10,000 PE and, in general, providing a good spatial coverage. The list with the WWTPs selected for the application at catchment scale is presented in Table 3.6.
Figure 3.17 represents average concentrations in the Adige main stem and its main tributaries for 2015 and separately for each pharmaceutical. Highest mean concentrations were detected for diclofenac, in particular in the southern and eastern part of the basin. The high concentrations in the upper parts of the Rienza and Avisio rivers may be justified by low dilution effects and high

Table 3.6: *List of the 26 WWTPs of the Adige River basin used for the simulation at catchment scale. The progressive number is associated to each WWTP and is a unique label also used in Figure 3.17.*

WWTP	**Province**	PE	**Progressive number**
Ala	Trento	10000	1
Rovereto	Trento	95000	2
Trento Sud	Trento	100000	3
Trento Nord	Trento	120000	4
Lavis	Trento	30000	5
Mezzocorona	Trento	26500	6
Campodenno	Trento	20000	7
Passo Tonale	Trento	10000	8
Tesero	Trento	50000	9
Mezzana	Trento	30000	10
Termeno	Bolzano	138000	11
Bronzolo	Bolzano	280000	12
Pozza di Fassa	Trento	40000	13
Bolzano	Bolzano	347000	14
S. Pancrazio	Bolzano	1500	15
Sompunt	Bolzano	49000	16
Bassa Valle Isarco	Bolzano	36000	17
Merano	Bolzano	360000	18
Sarentino	Bolzano	8750	19
Media Val Venosta	Bolzano	36000	20
Alta Val Venosta	Bolzano	30000	21
Passiria	Bolzano	14000	22
Wasserfeld	Bolzano	40000	23
Tobl	Bolzano	130000	24
Bassa Pusteria	Bolzano	40000	25
Wipptal	Bolzano	45000	26

input loads of contaminants associated to touristic presences whereas the high concentrations in the lower part of the Adige main stem may be due mainly to high input loads associated to the populated residential areas. Intermediate values were observed in the Noce upper stem and in the Adige river approximately at the municipality of Trento and at the borders

of the Provinces of Trento and Bolzano. Clarithromycin concentrations are the lowest in all the catchment; this is maybe due to the high coefficients of decay, in particular in winter, counterbalancing the negative combined effects of low dilution effects and high touristic presences. A part from clarithromycin, all other pharmaceuticals (i.e., ketoprofen, irbesartan and sulfamethoxazole) present low concentrations in the upper part of the basin except for the north-east (i.e., Rienza river), whereas concentrations become greater in the southern part (i.e., Noce river in the west and downstream the municipality of Trento).

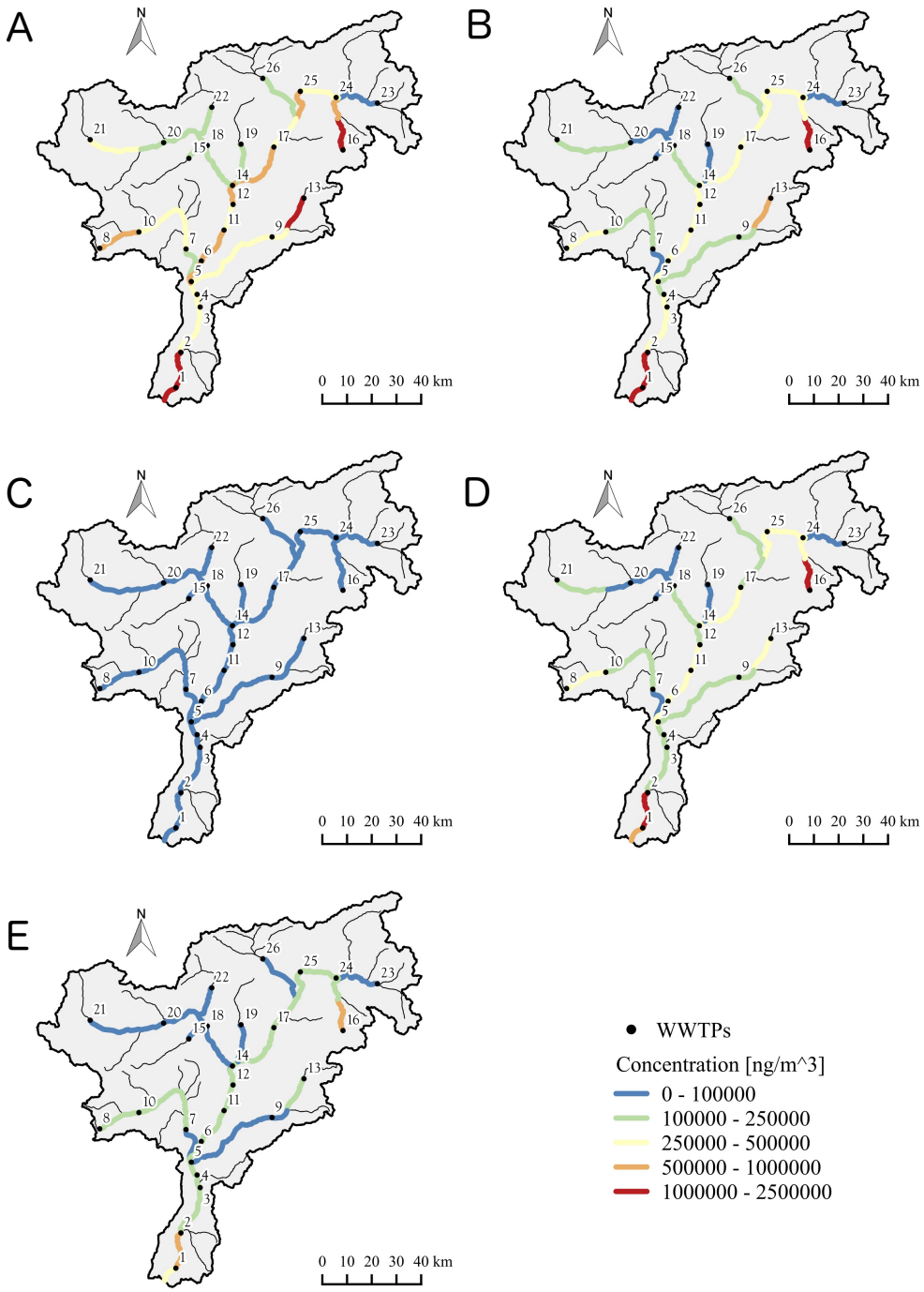

Figure 3.17: *River mean concentrations of (A) diclofenac, (B) ketoprofen (C) clarithromycin (D) irbesartan (E) sulfamethoxazole in the Adige catchment relatively to the year 2015. Points and the relative progressive numbers are associated to each WWTP included in the simulation. For the progressive numbers see Table 3.6. Blue colors represent low simulated mean concentrations (range of* $0-100\ ng/L$*) whereas red ones represent high simulated mean concentrations (range of* $1,000-2,500\ ng/L$*).*

In order to appreciate the variations of concentrations at monthly resolution and to evaluate the influence of the combined effects affecting concentrations (i.e., dilution, decay, dispersion etc.), temporal patterns of a selection of ten gauging stations both in the Adige main stem and in its tributaries is presented in Figure 3.18. As evidenced also in Figure 3.17, diclofenac is the most present pharmaceuticals in all the station and in all months whereas due to the higher coefficients of decay, claritromicyn is the lowest pharmaceuticals in all the station and in all months. The remaining pharmaceuticals present patterns similar to diclofenac but with lower concentrations: in particular, ketoprofen and irbesartan perform analogous concentration but lower if compared to diclofenac and to follow, sulfamethoxazole with low concentrations if compared to ketoprofen and irbesartan but higher if compared to claritromicyn. There are two contrasting patterns between different stations: at the gauging stations of "Avisio - Soraga", "Adige - Mezzolombrado" and "Adige - Ponte Adige", it is worth noting a peak of pharmaceuticals concentrations on summer that may be justified by an increase of pharmacological consumption in summer season, even counterbalancing the typical high dilution effect. Instead in all other stations, the combination of less dilution and low coefficient of decay evidences highest concentrations in winter. The only station that presents comparable peaks in summer and winter season is "Adige - Trento" (i.e. the gauging station is located at "Ponte S. Lorenzo" in the city of Trento). In contrast to other stations located in the upper part of the basin, the pharmaceutical input of the municipality of Trento is mainly due to resident population and it is less affected by touristic fluxes. In addition, the typical Alpine climate characterized by snow - melting in spring is evident in all the station and for all pharmaceuticals,

producing a local minimum in April and May and it can be justified with the increased dilution effect. These simulations showed that concentrations of pharmaceuticals change through the seasons with a behavior that depends on population dynamics and hydrological characteristics of the year: a behavior that cannot be identified when a single emissions and representative water discharge are adopted.

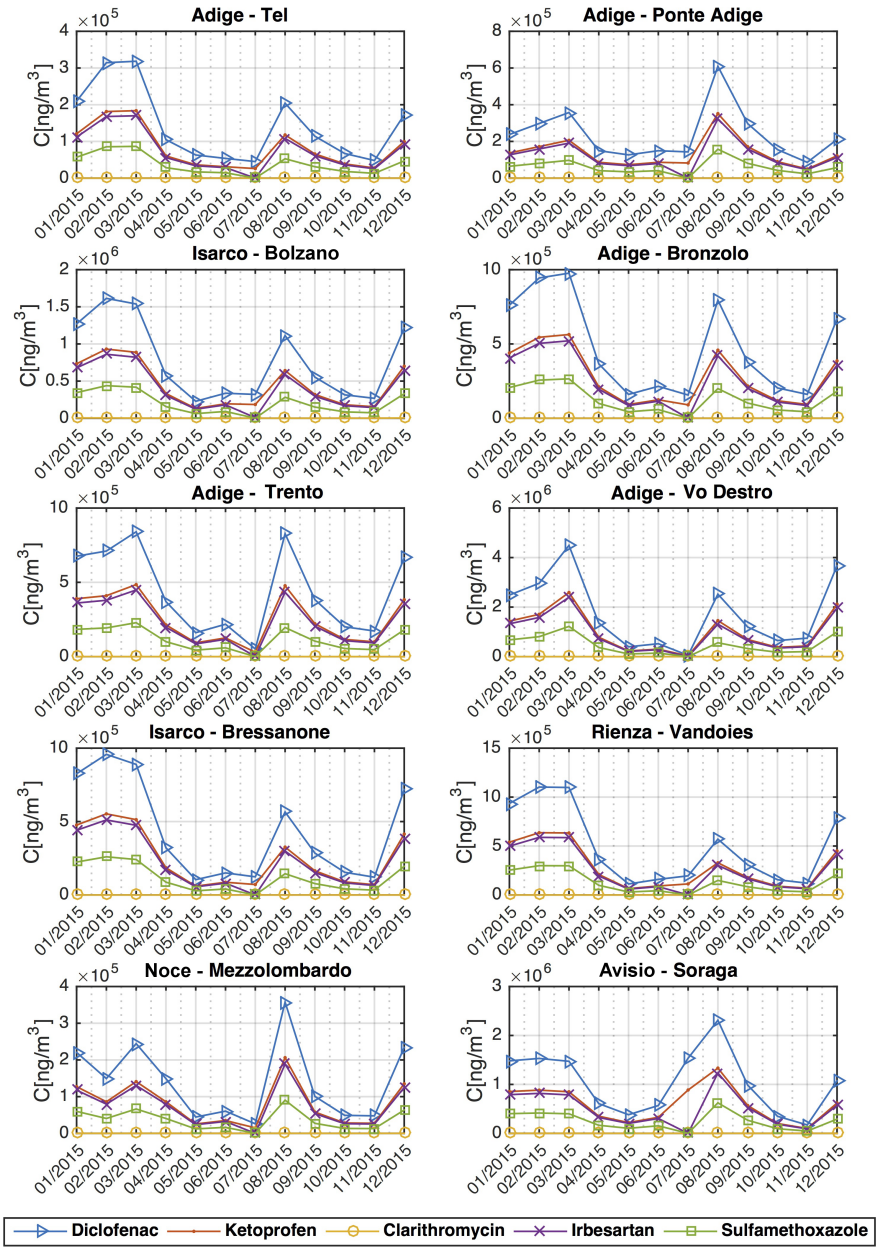

Figure 3.18: *Concentrations patterns of the 5 selected pharmaceuticals in 10 illustrative streamflow gauging stations within the Adige River Basin in the 2015. Different colors represent different pharmaceuticals.*

CHAPTER 4

CONCLUSIONS

4.1 Driver detection of existing water quality trends in the Adige, Ebro and Sava catchments

The first chapter of the thesis compares trends in water quality parameters of three large European river basins, characterized by different hydroclimatic and socio-economical conditions, and attempts to link them to the main drivers of change. The principal results of this study can be summarised as follows:

(*i*) Agriculture has been proved to affect BOD5, in particular for the Ebro, where the amount of organics in freshwaters is linked to the trends in the proportion of agricultural land use. Moreover, positive trends in PO_4 in the Sava are shown to be affected by increasing agricultural land use and thus likely by an increased use of fertilisers; instead, in the Ebro, downward trends may be explained by the reported reduced use of fertilisers and improvements in sewage treatment. It was additionally shown that agricultural practises also affect Cl and electrical conductivity in the

Sava, whose positive trends are probably due to the increase of agricultural activities and hence land run-off.

(*ii*) Population affects Cl in the Adige, where the recent increase in resident population, in particular in the north-western areas, has enhanced Cl emissions related to industrial activities, urban releases and use of road salt in winter. Additionally, BOD5 patterns in the Adige and Sava are shown to be correlated with population. Trends of PO_4 are, on average, positive for the Adige and are found to be correlated with population increase and thus with intensification of human activities.

(*iii*) The reduction of the dilution effect, mainly due to decreasing streamflow, is particularly evident in the Ebro and explains positive trends of Cl and electrical conductivity. Moreover, as expected, observed trends in DO are linked to both hydroclimatic drivers (i.e., Q_m and TA). Since DO is the variable presenting the largest number of negative trends in all the basins, an increasing risk of low DO is highlighted and it may have adverse effects on aquatic ecosystems, in particular in the Ebro, where downward DO trends are widespread and persistent.

(*iv*) TA, being a proxy of changing climate, is undoubtedly an important driver that influences mostly TW and DO. Due to the limited data availability and the absence of significant MK trends, only few positive trends in TW have been observed. However, increases in TA are found to be correlated with observed upward patterns of TW.

(*v*) The present work highlights the complex relationships between sources of pollution and water quality parameters, and demonstrates the importance of well-equipped and carefully managed monitoring networks.

Complementary to a deep understanding of the local system, statistical data analyses can represent a reliable tool for decision makers in river basin planning by providing them with an overview of the potential impact of ongoing climatic changes and river management policies on the aquatic ecosystem under investigation. We limited our analyses to few fundamental factors for which data are routinely monitored at the European scale, in order to implement statistical tools for data analyses. However, as there are numerous sources of water pollution, future studies might evaluate those at local scale and consider other compounds as indicators for diffuse pollution.

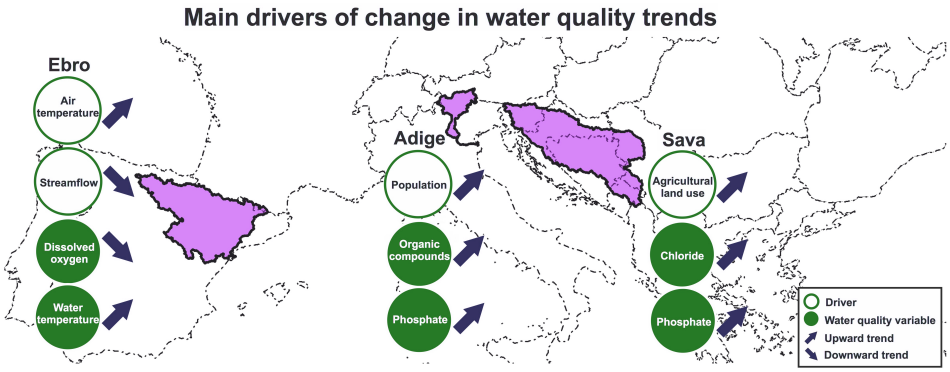

Figure 4.1: *Summary of the main results of the data analysis conducted in the three catchments.*

In addition to data collection and analyses, local emission models might be beneficial for a complete understanding of water pollution at river basin scale.

4.2 Contamination sources and distribution patterns of pharmaceuticals and personal care products in the Adige River Basin

Results of this second part of the thesis highlight tourism as a significant contributor to the overall PPCPs pollution of the

Alpine aquatic environment. The occurrence of PPCPs in Alpine rivers is associated with seasonal variation of river streamflow (low flow in winter and high flow in summer) as well as the fluctuation of tourist arrivals during the year. In the case of the Adige River, results show evidence of the strong tourism impact on the Alpine river quality. The concentrations of quantifiable PPCPs were typically in the ngL^{-1}-μgL^{-1} range, with detected values being in general higher during winter than during summer. This variation could be jointly attributed to low flow conditions, cold-water temperatures and increased number of tourist arrivals, especially in Val di Sole. Concentrations of selected PPCPs during winter in the downstream sites were significantly lower than in the upstream sites due to the higher streamflow (dilution effect) and lower number of tourist arrivals. During summer the pattern was reversed, and higher concentrations of PPCPs occurred in the downstream, a highly urbanized area of the basin. Nevertheless, despite the amount of the PPCPs data collected, the analysis of the available information would benefit from a complementary exploration of the ecotoxicological relevance of the PPCPs and their metabolites in the Alpine aquatic environment.

4.3 Transport model of micro and emerging pollutants

In this last part of the thesis, we presented an innovative transport model for simulating dissolved pharmaceutical concentrations in surficial waters. The model setup relies on the classical ADRE but introducing two original parameters: the theoretical load coefficient (γ) to synthesize WWTPs input and the seasonal coefficient of decay (k) that embodies the temperature dependence of biological processes causing

degradation. The model was tested on the Adige River Basin, in the North-East of Italy on a selection of five pharmaceuticals, accurately chosen from various chemical groups (i.e., analgesic/anti-inflammatory, antibiotic, antihypertensive): in particular, the inversion of model parameters was conducted on the Noce River Basin, one of the main tributary of the Adige river and then a prediction of the dissolved concentrations were performed in all the basin for a year (i.e., 2015) at monthly resolution. Preliminary simulations evidenced that the two main mitigation mechanisms were dilution and decay, overwhelming the dispersion effects at the catchment-scale. The calibrated model provides a good fit to the measured pharmaceutical concentrations, which is a promising result considering that no calibration has been carried out to optimize the boundary conditions and also considering the scarce availability of measures to test the model in other basins. Reliable predictions of monthly values of coefficients of decay for each pharmaceutical were obtained and the influence of touristic fluxes on solute concentrations can be noted and estimated in different areas of the basin under investigations. This ruling dependence of tourism and emerging contaminants concentrations hinders the possibility to eliminate population fluctuations in the estimation of pharmaceutical sources. The observed ranges of good parameters are case specific and their transferability to other basins has to be tested; however, an effective spatial transferability is also expected, owing to the easy possibility to couple the transport model to every existing hydro-climatological models. As expected, winter coefficients of decay are lower than the summer ones for every emerging contaminants: this is due to the temperature dependence of biological processes causing degradation. Among the five selected pharmaceuticals, diclofenac is the one mostly present

with low k. The same holds also for ketoprofen. In contrast, clarithromycin presents widely low concentrations mainly due to high k. All other pharmaceuticals concentrations range from 0 to $2,500 ng/L$ with maximum in the North-East and in the South of the Adige River Basin. Overall, the travel time formulation extended to a more complete framework that includes pharmaceutical solutes, touristic fluxes and resident population, positioning of WWTPs, water temperatures and seasonal variations of coefficients of decay, leads to an effective description of fate and transport of pharmaceuticals in rivers. Moreover, the proposed coupling with a generic hydro-climatological model yields promising results and can represent a new avenue for the pharmaceutical simulations at catchment-scale, which has interesting applications, especially in stream ecology.

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This doctoral thesis aimed at contributing with new insights into the multi-faceted aspects of solute transport at catchment-scale, proposing novel solutions, with applications to real-world case studies and including a detailed description of the major aspects that influence the water quality dynamics in rivers. In the first part, after a detailed description of three large European river basins (i.e. Adige, Ebro and Sava), a detailed data analysis of the main water quality variables is presented: advanced statistical analyses (i.e. Spearman rank correlation, Principal Component Analysis, and Mann-Kendall trend tests) were applied to long-term time series of water quality data both in the Adige River Basin and in the Ebro and Sava catchments, aiming at providing an integrated and comparative analysis of recent trends, in order to investigate the relationships between water quality parameters and the main factors controlling them (i.e. climate change, streamflow, land use, population) in the Mediterranean region. In the second part, sampling campaigns performed in the Adige catchment, are presented in detail. Special attention is also given to emerging pollutants, whose study on the occurrence patterns and spatiotemporal variability in the Adige River Basin has been conducted in conjunction with population patterns and touristic fluxes. In the third and last part, novel theoretical solutions of the well-known advection-dispersion-reaction (ADR) equation are presented. The theory was developed for both general water quality variables and pharmaceuticals, evidencing differences and analysing the main factors that influence water quality dynamics. An application is also proposed to the Adige catchment.

Elena Diamantini is graduated cum laude in both Civil and Environmental Engineering (BSc) at the Università Politecnica delle Marche and in Civil Engineering (MSc) at the Polytechnic of Turin, with a curriculum in Hydraulics. She wrote her Master thesis at the Technische Universität Wien, supervised by Prof. Günter Blöschl, in the field of flood change. During her PhD career, she developed both field work and computational modelling skills. Her research activities are connected with the European Globaqua Project, dealing with chemical stressors of freshwater environment. She is currently developing a catchment scale transport model of pharmaceuticals in rivers. She is author of many scientific publications on international journals and attended several national and international conferences and workshops.