

To: **Editor and Reviewers of the  
manuscript no. hess-2018-252**

Dear Editor and Reviewers,

The throughout reviews that we received contributed to improve the manuscript in several parts. Given this additional effort, we decided to involve Stefano Mallucci, who contributed making new simulations and participated in the revision of the manuscript. Given his contribution, both the authors of the original manuscript (Bellin and myself) feel that he deserves to be included as author. Therefore, according to the Editor and the Copernicus team, we ask for updating the list of the authors in the following order: Elena Diamantini, Stefano Mallucci and Alberto Bellin. We would be grateful for your understanding.

With sincere regards,

Trento, 25 October 2018

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NOTE: *Comments from the Reviewers are in BLUE and ITALIC.*

## Reply to Referee #1

### *COMMENTS FROM Referee #1*

#### *General comments:*

*This manuscript presents a simple approach to estimate concentrations of pharmaceuticals and personal care products (PPCP) in river networks through approximations of waste water treatment plant (WWTP) inflow and in-channel dilution. WWTP inflow is related to capita connected and thus an extrapolation to ungauged sites is theoretically possible, although the model requires local calibration to measured concentrations.*

*While the general novelty of this approach is understood, the present manuscript lacks an adequate description of existing knowledge and a model check with data that was not used for calibration. Since independent data obviously exists – i.e. was published in a preceding paper - such a model check is possible and would strongly contribute to the value of this research. Moreover, a large Lake of 180 mio m<sup>3</sup> exists in the middle of the examined river network but is neither shown nor mentioned or adequately discussed. Such a lake will certainly affect model results and probably also violate underlying model assumptions. Only if all concerns are adequately addressed, publication in HESS is warranted. I detail these concerns down below.*

#### **Reply**

We would like to thank the reviewer for evaluating our manuscript and for his/her valuable comments. Below we reply point by point to the reviewer's comments and illustrate the changes implemented in the revised manuscript.

To summarize, we address the three main concerns of the reviewer as follow:

**concern # 1)** *“the present manuscript lacks an adequate description of existing knowledge”*: we partially agree with this statement. We expand the discussion on the existing models, including also the one suggested by the reviewer. However, we do not agree that the existing knowledge was not adequately described in the original version of the manuscript as explained below in the answer to the specific comment by the reviewer;

**concern # 2)** *“effect of the lake”*: we deal with this important point raised by the reviewer as explained below by expanding our model's description to include the effect of reservoirs and lakes to demonstrate its flexibility in dealing with impacted catchments;

**concern # 3)** *“a model check with data that was not used for calibration”*: Unfortunately we cannot make the validation suggested by the reviewer. The

additional data he/she mentions are very few and most importantly we cannot perform for these points simulations at the daily scale because only monthly touristic presences are available for the Adige catchment, except in the Noce river where we collected also touristic presences in the days of the sampling campaigns. However, we make a qualitative comparison of the spatial and seasonal patterns showed by the simulations with the observations after warning the reader of the time scale mismatch between simulations and measurements.

In his/her comments the reviewer focuses on specific aspects of the example that we used to illustrate a possible application of the model. This was very useful to us to identify points where our presentation needed an improvement. However, without reducing the importance of these valuable comments, we feel that the most relevant contribution of our manuscript is not the application per se, but the model we present which we believe contains elements of innovation worth to be discussed. We add a sentence in the presentation of the applications specifying that the simulations are intended to identify most impacted sites and seasonality of the concentration (in relative terms) rather than making an accurate prediction of the concentrations at the sampling points; which is the following: “It should be acknowledged that model's parameters are affected by uncertainty, which is expected to be large due to the limited number of data available for inference. For this reason the results of the simulations discussed here should be considered as a preliminary exploration providing uncertain estimates of concentrations at the sampling points. However, the simulated spatial pattern of the concentrations and its relative values are much more reliable than the absolute concentration at a given point, such that areas where the impact of PPCPs is stronger are reliably identified.”

### *Specific comments:*

#### *1. Existing knowledge: Concentrations of PPCPs*

*The paper lacks a description of existing studies on the occurrence and spatio-temporal dynamics of PPCPs in European rivers. In recent years several studies have been published in various river systems. This is important, because the results of the present studies should be compared to other regions to prove that both measured and simulated concentrations are realistic. I propose a table in the introduction where the five simulated compounds are selected and occurring concentrations are given for different rivers. Those should be used to evaluate model quality in the discussion. By the way: it is not true that PPCPs are not measured on a regular basis by environmental agencies: At least in the Rhine River measurement stations exist for this purpose (e.g. in Weil, check at: <http://www.aue.bs.ch/umweltanalytik/rheinueberwachungsstation-weilam-rhein.html>)*

### **Reply**

We partially agree with this comment. From one side including a table with examples of concentrations measured worldwide may be useful to evidence the relevance of the issue and the need for robust modelling approaches. On the other hand, we disagree with the comment that concentrations measured in other rivers may validate the measurements we used in the present work, since they depend on the amount of population, type of the water treatment and other factors that are site (catchment) specific. The quality of the measurements we used in the present work is granted by the protocols used in the sampling campaign, the care in maintaining and shipping the samples, and the analytical methodologies used in the lab. All this is discussed in previously published papers and therefore we add a sentence at page 12 and lines 11-14, specifying the care with which all the operations have been performed referencing to the work by Mandaric et al. (2017) for details. As for the sentence “PPCPs ... are not monitored on a regular basis by environmental agencies” we were meaning that a regular monitoring is not yet enforced by regulations at the European level. This does not prevent agencies of member states to introduce independent monitoring activities, continuous or not, for specific compounds. To accommodate for the above comments we add the table suggested by the reviewer in the Introduction section (at page 5 of the revised manuscript) and the following sentences: 1) “The quality of the measurements utilized in the present work is granted by the protocols used in the sampling campaign, the care in maintaining and shipping the samples, and the analytical methodologies used in the laboratory. For further details on the protocols followed in sampling, handling, shipping and analyzing the samples, we refer to the previous work of Mandaric et al. (2017)” at page 12 and lines 11-14; and the sentence 2) “Despite these substances are ubiquitous in populated areas and detected in fresh waters with concentrations ranging from nanograms to micrograms per litre, a regular monitoring activity by Environmental Agencies is not yet enforced by regulations at the European level” at page 1 and lines 15-18 of the revised manuscript.

## *2. Existing knowledge: Model approaches*

*The literature overview at the end concentrates on two, relatively similar GIS-based model approaches, GREAT-ER and PhATE, that are both more than ten years old. More recent approaches are missing, e.g. the study of Osorio et al (2012) who applied a simple plug-flow model to simulate pharmacologically active compounds in the Ebro river taking into account different dilution by varying flow conditions and an overall decay constant. They also determined decay constants for ibuprofen, furosemide, enrofloxacin, enalapril, acetaminophen, diclofenac and ketoprofen. So the authors should state why they developed a new model and what are the differences and benefits of their approach. Finally they should also compare their calibrated decay constants to those by (Osorio et al. 2012).*

## **Reply**

We thank the reviewer for this comment. We considered PhATE and GREAT-ER as the state of the art because, to our best knowledge, they are the most comprehensive and used models available in literature. In addition, they have been applied and developed in recent years by several authors (among others, Aldekoa et al., 2015 for PhATE and Kehrein et al., 2015 for GREAT-ER). Other models (e.g., Scheytt et al., 2006; Morales et al., 2007; Einsiedl et al., 2010; Vulliet et al., 2011; Osorio et al., 2012, Vione et al., 2018) share with GREAT-ER the conceptual framework, which is less general with respect to our model, particularly for what concerns the hydrodynamic processes. For example, the model presented by Osorio et al. (2012) does not take into account the change of velocity and the increase of dilution along the path from the source to the detection section. This is evident in the structure of the equations (4) and (6) of the paper by Osorio et al. (2012), which are used to estimate the residence time of the path from the source to the control section by using a single constant water discharge. This is legitimate if the distance from the source to the control section is such as the water discharge (i.e. the contributing area) changes little along the path, as admitted in the lines following equation (2) of the paper by Osorio et al. (2012). However, the validity of this approximation can be questioned in most applications dealing with multiple sources on a network. In Osorio et al. (2012) the effect of multiple sources is taken into account by rescaling the residence time with the annual volume of the sources as shown in equation (5). This rescaling is empirical. In our model we take into account both effects in a rigorous manner. Stream velocity changes stepwise along the network as the result of considering the water discharge constant along the single reach but changing from node to node according to the contributing area. In this framework dilution along the path is considered by performing mass balance at the nodes of the network. The effect of multiple sources is addressed in a rigorous manner by taking advantage of the linearity of the transport equation (see the presentation of the model). We believe that these characteristics are a significant improvement of the existing modelling approaches, including that referenced by the reviewer. Notice that neglecting dilution along the path may result in a severe overestimation of the concentration or, in case of calibration with observed concentrations, in a decay coefficient larger than the real one to compensate for unmodeled dilution. All these processes, not considered in previous approaches, are introduced in a simple, yet rigorous, manner in our modelling approach. We expand the discussion of the advantages of our approach with respect to the existing ones in the introduction section (from line 5 of page 3) of the revised manuscript.

### *3. Missing information about model boundary conditions*

*How was the weather (rainfall, air/water temperature, etc.) during the two sampling periods? Since water temperature and discharge are two main parameters that influence the model results, this information is crucial to evaluate the model results. If figure 3 of Mandaric et al. (2017) is considered, the runoff difference between the sampling campaigns of February and July is rather small for the two downstream*

*sites WB4B and WB5B. Here absolute numbers should be presented in a table, in addition to weather conditions and air/water temperatures.*

### **Reply**

We comply with the reviewer's request of providing information on meteorological and hydrological conditions during the sampling campaigns. Hence, we introduce a table with the available meteorological and hydrological data (i.e. water temperature and streamflow) in the subsection 3.2. For what concern rainfall data, we specify that the first sampling campaign was conducted in the dry season (winter) and the second in the period of snow melting (summer). However, in both campaigns no significant rainfall was detected during the sampling operations and in the previous days. We remark here that the model is structured in such a way that the effects of water discharge and temperature are automatically considered in the simulations. All the available information of measured data were already published as supplementary data in the Appendix of Mandaric et al. (2017), to which we refer for further information.

### *4. Missing information about Lake di Santa Giustina*

*A more accurate map of the study catchment is required. Unlike in the preceding paper, an existing large lake between upstream (WB3A and WB3B) and downstream (WB4B and WB5B) sites is not shown in the catchment map and even not mentioned in the paper. Why? This lake of 180 million m<sup>3</sup> volume will largely increase residence times and mixing and certainly affect model results. This could also explain differing model results between the upstream and downstream stations. Moreover, such a large lake has impacts on various simplifying model assumptions, as discussed below. Here an extensive discussion is needed including a quantitative estimate on the solute residence times in the lake (at different discharge conditions).*

### **Reply**

We thank the reviewer for noticing this. We change the figure as required. Concerning the second, more important, comment one may note that in principle natural lakes and reservoirs can be easily implemented in our modelling framework by adding the pdf of its residence time into equation (12). However, from the application point of view, the selection of a proper residence time pdf requires information on hydrodynamic characteristics such as the distribution of the residence times and the type of micro-mixing, which we did not find at a first inspection of available information on the S. Giustina reservoir. Since we agree with the reviewer on the importance of the reservoir for the downstream sampling points, we performed a throughout analysis of available reports and elaborated a simplified, yet accurate, model of the reservoir. A first consideration is that the reservoir is in between sections WB3B and WB4B and shows a significant increase of the contributing area with respect to the former section. In the current approach we introduce the hypothesis of perfect mixing, which entails that the outflows sample ages proportionally the volume-weighted distribution of ages available in the reservoir. These changes

required to perform again both the calibration and the simulations over the entire Adige river. To comply, and we think to resolve the issue raised by the review, we make the following changes to the original manuscript: 1) modify the description of the Adige catchment in the subsection 3.1 (from line 24 of page 10 to line 13 of page 11) by adding a detailed description of the reservoir and the residence times as follows: “The Noce river is exploited for hydropower production with 4 reservoirs, two in the upper course (Careser and Pian Palù) and two in the middle course (S. Giustina and Mollaro). Careser and Pian Palù are in headwaters with no WWTPs upstream and therefore they enter in the model only with their effect on the water discharge. The other two are downstream of a few WWTPs (see Figure 2 and Table B1 in the Appendix B) and therefore their effect on the residence time is included. The Mollaro reservoir is just downstream of the S. Giustina reservoir and since no release points are in between we merged them in a single equivalent reservoir. A recent publication of the Hydrological Observatory of the Trento Province (2007) shows that in the period 2001-2005 the average volume stored in the S. Giustina reservoir was of  $12.089 \cdot 10^6 \text{ m}^3$ . In the same period the mean water discharge was  $25.8 \text{ m}^3 \text{ s}^{-1}$ , thereby leading to a mean residence time of  $\tau_{s_1} = \frac{\bar{V}}{\bar{Q}} = 53.7 \text{ days}$ . Mollaro has a little storage volume compared to that of S. Giustina. At the maximum storage (i.e.,  $0.860 \cdot 10^6 \text{ m}^3$ ) the mean residence time is of  $\tau_{s_2} = 0.38 \text{ days}$ , which summed to the mean residence time of S. Giustina leads to a total residence time of the two reservoirs of  $\tau_s = \tau_{s_1} + \tau_{s_2} = 54 \text{ days}$ . Notice that the storage of Mollaro has been considered constant because of its small volume which allows very little flexibility for storing the water released from the S. Giustina reservoir (the S. Giustina reservoir feeds the Taio power plant which release point is just upstream of the Mollaro reservoir) and counts only for a small fraction of the total residence time of the two reservoirs. In this situation the water coming from S. Giustina and the small catchment between the two reservoirs is stored for a very short time in the Mollaro reservoir with respect to the residence time of S. Giustina, such that fluctuations of its storage volume are not influencing significantly  $\tau_s$ ”; 2) modify Figure 2 according to reviewer’s suggestion; 3) modify equation (12) at page 7 to include the effect of lakes and reservoirs (namely by adding the pdfs of the lakes to the convolution) and by adding the following text at page 9 and lines 25-28, after equation (15): “If a lake is encountered along the path and its functioning can be represented as a plug-flow such that  $g_M(s_k, t) = \delta(t - \tau_{s_k})$ , Eq. (15) should be generalized by adding the residence time  $\tau_{s_k}$  (and that of the other lakes encountered along the path) to the channels residence times  $\tau_{i,j}$ . If the hypothesis of plug-flow does not hold, the pdfs of all the lakes encountered along the path should be convoluted to the Eq. (15)”.

## 5. Model assumptions

*Limitations caused by the following model assumption need adequate discussion: a.) the model only accounts for point sources. How large is the error by diffuse sources, e.g. sewer overflows during large rainfall events, manure use, etc. b.) the entire*

*concept is based on the hypothesis that the scale of interest is larger than the residence time. Does this hold, especially regarding the big lake? c) can velocity be assumed to be spatially uniform within the channels (p 4)? Generally it seems more plausible that flow velocities are higher in steep headwaters and again, what about the lake? d) also the assumption that local dispersion is overwhelmed by geomorphological dispersion is problematic if one thinks about a large lake. e) how realistic is the assumption that every WWTP is equally efficient, i.e. has the same decay factor (p. 10)? From my experience there are large differences depending on the size of the WWTP, on its age and used techniques. Snip et al. (2014) exemplified the effect of different operation conditions on WWTP efficiency regarding PPCP removal. f) was the water temperature really constant throughout the network and throughout the three-day sampling campaign? Here again the balancing effect of the lake might play a role. Real measured data needs to be presented here (see 3. above).*

## **Reply**

We thank the reviewer for these comments. We will answer to each point in the same order.

- a) Our model is based on a segmentation of the path from the source to the control section with the source that is introduced at the location where the WWTP discharges into the river. Therefore, diffused contributions can be evaluated at the level of the sub-catchment draining into the reach and treated as a point source located at its middle point. The details to which the variability of the diffused contribution is considered is controlled with the drainage density (i.e. the density of the network) and in many cases this is a better approximation of the diffused contribution than assuming (arbitrarily) a uniform distribution, which however can be handled if needed simply by assuming the same diffused specific load in each sub-catchment. We comment this point in section 2.1 of the revised manuscript (page 9, lines 4-11) as follows:

“Notice that the model is based on a segmentation of the path from the source to the control section. Therefore, diffused contributions can be evaluated at the level of the sub-catchment and treated as a point source located at the middle of the channel draining the sub-catchment. The length of the channels composing the river network, and therefore the size of the sub-catchments can be varied according to the threshold in the contributing area chosen during the identification of the river network from the Digital Terrain Model (see e.g. Rodriguez-Iturbe and Rinaldo, 1997). Hence, the maximum detail with which the spatial variability of the diffused contribution is reproduced can be controlled by the modeler simply by changing the density of the network. Notice that this has also an effect on the minimum time scale at which variability of the flow field can be captured, through the control of the channel length on the residence time.”

For the case at hand, sources of diffused origin are not relevant since the region uses separate sewer systems, which eliminate sewer's overflow and the possible input from manure cannot be evaluated with the information available. We add the following caveat in Section 4 (from line 31 of page 13 to line 1 of page 14): "To comply with Occam's razor principle (MacMay, 2003 ch. 28), suggesting parsimony in selecting model complexity and considering the very limited amount of concentration data available, the parameters in the Eq. (13) are assumed the same for all the WWTPs and since  $\gamma$  is inferred the abatement  $f$  is assumed to be zero. This simplification is supported by the fact that all WWTPs of each of the two provinces are managed by the same agency by using similar technologies".

- b) This is not what we meant and also in this case one should separate the characteristics of the models, and the processes it includes, with the approximations introduced for the case at hand. The approximation introduced applies to equation (2), which refers to the single reach not to the entire pathway as the reviewer implicitly assumes. In this context what we require is that the residence time in the single reach is smaller than the characteristic time of change of water discharge. In a single reach the residence time may vary between minutes to hours, thereby the approach may be questioned only during flooding events. We are currently exploring what we "lose" by using this parsimonious approach also during flooding events, but discussing this is beyond the scope of the present work. At the level of the entire network the effect of a water discharge changing in time is addressed by means of equation (10). In the application, we introduced the further hypothesis that the ratio of water discharges in equation (10) can be approximated as the ratio of the contributing areas, which is a reasonable assumption in normal hydrological conditions (no flooding) as actually was the case during the sampling campaign. This is an approximation that is instrumental to simplify the computations given the type of data available but can be removed in applications if the data available allow to do it. For what concerns the reservoir the assumption is that fluctuations of the water discharge influence little the residence time, which depends on the ratio between the mean stored volume and the mean water discharge at the monthly or seasonal scale, depending on the data available. Again, our modelling approach is flexible enough to tailor the complexity of the model to available data and modelling goals. We are not saying here that modelling should be adapted to data available, rather that there should be a balance between modelling goals investment in data collection and modelling effort. We introduce in section 2 at page 4, lines 17-21, a caveat to better specify this point: "The model assumes that the velocity is steady state, but it can be used to simulate representative states of a slowly variable flow approximated as the superimposition of a sequence of steady state velocity fields. This is acceptable if the characteristic time of water discharge variations is larger than

the residence time within the channel. Considering the typical length of the channels composing a river network and the time scales at which the PPCPs loads are available, time variability can be captured at daily or larger time scales”.

- c) In equation (2),  $v$  is the mean channel velocity and the effect of spatial variability of point velocity within the channel is taken into account by the diffusivity  $\alpha_L$  introduced in the pdf (equation 6) of the travel time. It has been shown in the past (Rinaldo et al., 1991) that at the network level the effect of  $\alpha_L$  on the shape of the hydrological response is negligible compared to the morphological dispersion reflecting dilution occurring at the nodes of the network and this justifies the approximation of  $\alpha_L \rightarrow 0$  introduced in the equation (15). Notice that the velocity is spatially constant within the single reach, but varies along the network according to the scaling law introduced by Leopold (1953) and recently elaborated further by Dodov and Foufoula-Georgiou (2004) (see equation 3 and appendix A). According to these scaling laws, the velocity varies slightly along the network and increases moving downstream, as the contributing area increases, rather than reducing as argued by the reviewer. This is a well known result of early studies on river morphology that our model takes into account. A lake or a reservoir is a storage unit and therefore its functioning is different from that of a river. In particular, the reservoir is modelled with a transfer function that depends in a complex manner from reservoir hydrodynamics, which is typically epitomized through a relationship relating residence time and stored volume. This differs from a reach, where kinematic mechanisms, epitomized through the velocity, prevail over storage mechanisms. We specify how we implemented the reservoirs in the subsection 2.1 from the page 7 to 9 (see the reply to comment 4).
- d) We do not understand this point. Local dispersion refers to streams, while the pdf of the residence time in lakes or reservoirs enters in the definition of geomorphological dispersion by increasing it. So the presence of the reservoirs makes this assumption even more accurate than in case of a network without them.
- e) As before, we divide the answer to this question into two parts; what the model can do and what the available data actually permit. The efficiency of the WWTPs is included in our model through the decay coefficient  $f_i$ , which is compound specific and may change depending on the treatment technology. In the application we do not estimate  $f_i$  just because it enters into the parameter  $\gamma_i$  (see equation (13)), which is calibrated after assuming that all the WWTPs have the same efficiency. This is acceptable for the case at hand since all the WWTPs of the province of Trento are managed by the same public authority, which guarantees uniformity in the conduction, and the employed technology is the same. Similar considerations can be made for the

WWTPs of the Bolzano province. We remark that the choice of the parameters that are not subjected to calibration (fixed) depends on the particular application and that in other situations, for example when  $f_i$  is known, a different choice can be done. This is not by any means a limitation of the model, which as we said can handle the case of  $f_i$  variable if needed and if proper data are available.

f) Yes water temperature is nearly constant, as can be seen in the Table 2 of the revised manuscript showing the relevant meteorological data during the sampling campaign (see the reply to the comment n. 3).

## 6. Model check

*Apart from the missing incorporation of the big lake, this is the main criticism of the presented approach: a missing model check with independent data. In the chapter 4 the model is extrapolated to the entire Adige river catchment and the spatial (Figure 5) and temporal (Figure 6) dynamics of selected components are shown. But how realistic are these results? Here the authors miss the chance of an independent model check. In their preceding paper Mandaric et al. (2017) presented additional data of the Adige catchment upstream the inflow of the Noce and downstream the town of Trento. This data could be used for a real model check and compared to simulated concentration WITHOUT re-calibrating the model.*

## Reply

We thank the reviewer for this comment. Unfortunately we do not have enough data for a formal validation and, in addition, for sampling points along the main stem of the river Adige (WB6 and the four sites labelled WB7) census data of touristic presences are available only at the monthly time scale. However, these data allows a qualitative check based on the comparison of the spatial and temporal pattern seen in the data and obtained with the simulation. On the other hand a one to one comparison of the measured and simulated concentration may be misleading for the reason just discussed. To evidence this we add the following sentence at the beginning of section 5 (page 19, lines 16-20), specifying the use that can be done of the results of the simulations, which are intended to demonstrate a possible application of the model with the limitations due to the type of available data rather than the model itself: “It should be acknowledged that model's parameters are affected by uncertainty, which is expected to be large due to the limited number of data available for inference. For this reason the results of the simulations discussed here should be considered as a preliminary exploration providing uncertain estimates of concentrations at the sampling points. However, the simulated spatial pattern of the concentrations, and in particular their relative values, is much more reliable than the absolute concentration at a given point, such that areas where the impact of PPCPs is higher are reliably identified”. In the same section, at page 21 and lines 3-10, we add the following sentences referring to the use of the additional information to which the reviewer refers in his/her appraisal: “During the two sampling campaigns samples were

collected and concentrations evaluated at the sites WB6, just upstream of the city of Trento and the confluence of both Noce and Avisio, and at four locations labelled WB7 A, B, C and D, downstream of Trento (see Mandaric et al. 2017 for location). This additional information cannot be used for a formal validation because representative of the sampling day, while simulations are conducted at the monthly scale because along the mean stem of the Adige river census data are available only at this scale for the touristic fluxes and at the annual scale for the resident population. While one can safely assume that resident population changes little within a year, touristic fluxes show significant variations at the weakly and even shorter time scales. Monthly concentrations produced by the model at selected sections are discussed below keeping in mind this limitation.”

### *7. Model description*

*A large part of the present manuscript consists of a presentation of the applied model approach, model selection and calibration strategy. The model description is lengthy and should be condensed. The section 2 “model” should be included into the section “material and methods”. Here the model development itself should be described in a first subsection followed by parameterization and calibration strategies. Most of the equations should be moved into the annex, and figure 1 be omitted.*

#### **Reply**

We disagree with this reviewer’s comment. Our intention is not here to present the data of a sampling campaign, and model them with an existing modelling approach, but rather to present a new model. With this objective in mind, we believe that the description of the model should be detailed enough to show the differences with existing approaches and discuss prons and cons of the proposed approach. Figure 1 is important to discuss the conceptual framework and therefore we decide to keep it.

### *8. Code and data availability*

*The sampled data should be provided as a table in the annex (upon publication the data is already published twice). Also the model code could be provided as an executable file.*

#### **Reply**

We thank the reviewer for the comment. All sampled data were already available online in the Appendix of Mandaric et al. (2017) and are easily accessible (the publication is open access) and we think there is no need to replicate tables here. Again, our objective is not to publish data, which have been already published as mentioned by the reviewer, but to present a new modeling approach. The model code is available upon request as declared at the end of the revised manuscript.

*Technical corrections:*

*The entire manuscript needs a thorough language check by a native speaker. Internet-Links should be omitted from the main text.*

## **Reply**

We thank the reviewer for the suggestion. We check carefully the English language and we omit internet-links from the main text.

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## **Reply to Referee #2**

### *COMMENTS FROM Referee #2*

*The manuscript describes a model of transport of contaminants in surface water. Specifically, five pharmaceuticals (diclofenac, ketoprofen, clarithromycin, sulfamethoxazole and Irbesartan) are modelled in a case study application. The proposed framework is original and the main innovative contribution is related to the stationarity hypothesis and to the number of parameters. The manuscript is well written and pleasant to read. The model is appropriately described and the case study is rich of information. Results are promising and the proposed model represents an interesting amelioration compared to the previous ones present in literature. I have only a minor suggestion, that is, to improve the figure 3 (first line: diclofenac) since apparently it is not clear that there are also blue points under the red ones.*

### **Reply**

We thank the Reviewer for his/her appreciation of our work. We improve figure 3 by substituting the bullets with other symbols.



# A parsimonious transport model of emerging contaminants at the river network scale

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**Abstract.** Waters released from wastewater treatment plants (WWTPs) [<sup>1</sup>] represent a relevant source of pharmaceuticals and personal care products to the aquatic environment, since many of them are not effectively removed by the treatment [<sup>2</sup>] systems. The consumption of these products increased in the last decades and concerns have consequently risen about their possible adverse effects on the freshwater ecosystem. In this study, we present a simple, yet effective, analytical model of transport of contaminants released in surface waters by WWTPs. Transport of dissolved species is modeled by solving the Advection-Dispersion-Reaction Equation (ADRE) along the river network by using a Lagrangian approach. We applied this model to concentration data of five pharmaceuticals: diclofenac, ketoprofen, clarithromycin, sulfamethoxazole and irbesartan collected [<sup>3</sup>] during two field campaigns, conducted in February and July 2015 [<sup>4</sup>] in the Adige river, North-East of Italy. The model showed a good agreement with measurements and the successive application at the monthly time scale highlighted significant variations of the load due to the interplay between streamflow seasonality and variation of the anthropogenic pressure, chiefly due to the variability of touristic fluxes. Since the data required by the model are widely available, our model is suitable to large-scale applications.

## 1 Introduction

The presence of pharmaceuticals and personal care products (PPCPs) in the environment raises growing concerns because of their potential harmful effects on humans and freshwater ecosystems (Ebele et al., 2017). Despite these substances are ubiquitous in populated areas and detected in fresh waters with concentrations ranging from nanograms to micrograms per litre [<sup>5</sup>] (see e.g., Table 1), a regular monitoring activity by Environmental Agencies is not yet enforced by regulations at the European level (Heberer, 2002; Ellis, 2006; Kuster et al., 2008; Acuña et al., 2015; Rice and Westerhoff, 2017). The main entry route of PPCPs into the aquatic environment is through the water discharged by [<sup>6</sup>] Waste Water Treatment Plants

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(WWTPs), whose removal efficiency varies in dependence of the type of contaminant and the treatment technology (Halling-Sørensen et al., 1998; Rivera-Utrilla et al., 2013; Petrovic et al., 2016). The ubiquitous presence of PPCPs in freshwaters is due to the rise of urban population and the continuous introduction of new products in the market, given the escalating request by human population and for livestock breeding. Persistence of PPCPs in freshwater varies from a few days to years, depending on both environmental conditions and characteristics of the compound. However, their concentration downstream of the WWTPs may change significantly as an effect of dilution and environmental conditions, chiefly solar irradiation and water temperature. Situations of pseudo-persistence of supposedly rapidly degrading PPCPs due to <sup>[..<sup>7</sup>]</sup>multiple release have also been observed (Ebele et al., 2017).

Since PPCPs are designed to exert physiological effects at low dosage, possible adverse consequences on humans and biota have become an issue of increasing concern (Heron and Pickering, 2003; Schwab et al., 2005; Boxall et al., 2012): disruption of human endocrine functions, developmental defects in fish and other <sup>[..<sup>8</sup>]</sup>organisms, alterations in the survival, growth, and reproduction of several species, and the promotion of antibiotic resistance are just a few examples of adverse effects requiring investigation (see e.g., Brooks et al., 2009; Corcoran et al., 2010; Hemond and Fechner, 2014; Ebele et al., 2017). As a first response to these concerns, the European Union emanated the Directive 2013/139/EU (Council of European Union, 2013) which identifies priority substances that might represent a potential risk and defines environmental quality standards.

<sup>[..<sup>9</sup>]</sup>Specific modeling approaches have been proposed with the objective to evaluate the propagation of PPCPs in <sup>[..<sup>10</sup>]</sup>rivers (see e.g., Scheytt et al., 2006; Osorio et al., 2012; Vione et al., 2018) all sharing the conceptual framework of GREAT-ER (Geography-Referenced Regional Exposure Assessment Tool for European Rivers) (Feijtel et al., 1997) <sup>[..<sup>11</sup>]</sup>and PhATE (Pharmaceutical Assessment and Transport Evaluation) (Anderson et al., 2004). Both are GIS-based models and take into account the decay of the species along the river in a simplified manner by considering a representative water discharge and therefore neglecting changes of dilution due to its variability in time.

<sup>[..<sup>12</sup>]</sup>PhATE applies mass balance at the catchment scale <sup>[..<sup>13</sup>]</sup>after having lumped all the releases upstream the point of interest and <sup>[..<sup>14</sup>]</sup>then estimates the concentration of a target compound by dividing the total WWTP load by a representative water discharge (Anderson et al., 2004). <sup>[..<sup>15</sup>]</sup>The model is composed of two modules: the exposure module, which estimates environmental concentrations, and the human health effect module, which <sup>[..<sup>16</sup>]</sup>is intended for risk assessment (Aldekoa et al., 2015). <sup>[..<sup>17</sup>]</sup>The effect of transport along the river network is therefore neglected and the water discharge is typically selected

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as representative of low flow conditions [..<sup>18</sup>]such that seasonal variations cannot be assessed. The WWTP loads are estimated [..<sup>19</sup>]by multiplying the total compound consumption, given [..<sup>20</sup>]as the product of the per capita consumption [..<sup>21</sup>]and the served population, by two reducing factors taking into account the fraction of the compound metabolized by the human organism and that removed by the WWTP.

5 GREAT-ER was developed for applications in large river basins at the pan-European scale (Boeije et al., 1997; Koormann et al., 2006), [..<sup>22</sup>]but it has been [..<sup>23</sup>]applied also for environmental risk assessment (Kehrein et al., 2015). The river network is divided into connected segments, each one receiving the load from upstream and from both the WWTPs and the industrial sewage systems directly connected to it. The last version of the software includes a uniformly distributed injection along the segments (Kehrein et al., 2015). The model assumes stationary (constant in time) emissions such that residence  
10 time is relevant only if decay is considered. Several types of decay are included, all lumped in a first order kinetic with the residence time estimated as the ratio between the length of the segment and a reference stationary flow velocity. Similarly to PhATE, and consistently with the hypothesis of stationary release, a single water discharge representative of low flow conditions is considered to obtain concentrations from the estimated mass flux. Stationarity of emissions and the assumption of a constant and deterministic residence time does not allow to estimate the seasonal variability of PPCPs concentrations  
15 at the selected locations. However, recognizing that uncertainty plagues parameters selection, and in an attempt to evaluate its propagation to the concentration estimates, the developers of GREAT-ER included a Monte Carlo procedure to evaluate parametric uncertainty under the assumption that the parameters are normally distributed independent random variables with given means and variances.

[..<sup>24</sup>]In the present work we propose a new modeling [..<sup>25</sup>]framework which includes hydrodynamic processes and  
20 dilution occurring along the river network in a rigorous, yet simplified, manner while keeping the model parsimonious in term of number of parameters. Differently from existing models, our approach takes into account flow variations along the path from the source to the point of interest, by assuming that water discharge changes at the nodes of the network while remaining constant along the edges (streams) connecting the nodes. In doing that water discharge, and therefore stream velocity, varies stepwise along the path from the source to the point of interest and dilution is included by performing  
25 mass balance at the nodes of the network. Moreover, multiple sources are addressed in a rigorous manner by taking advantage of the linearity of the transport equation simply by adding all the contributions after their transfer to the control section (see Sect. 2). Our model removes the assumption of stationarity in both emissions and streamflow. In the present work transient flow conditions are modeled as a succession of stationary flows representative of seasonal variability, under the hypothesis that the residence time along the edge is smaller than the characteristic time of flow variations. This hypothesis

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can be removed at the price of a <sup>[..<sup>26</sup>]</sup>higher model complexity, which is not always justified, particularly when the objective of the analysis is the estimation of the seasonal loads, as in the present work and in most applications alike. <sup>[..<sup>27</sup>]</sup>Including variability of flow and releases, though in a simplified manner, is important in all the cases with seasonal fluctuation of water discharge and populations, the latter due to touristic fluxes, such as in the Alpine region. Indeed, the importance of <sup>[..<sup>28</sup>]</sup>seasonality in PPCPs consumption and streamflow may be limited in large pan-European catchments (in particular the former) but becomes more influent as the size of the catchment reduces, especially in the Alpine region where touristic fluxes causes relevant seasonal variations of the population. The effects of the above <sup>[..<sup>29</sup>]</sup>variabilities have been scarcely investigated (see e.g., Alder et al., 2010), since very few studies have analyzed temporal and seasonal variations <sup>[..<sup>30</sup>]</sup>in both concentrations and overall attenuation of PPCPs loads <sup>[..<sup>31</sup>]</sup>(Loraine and Pettigrove, 2006; Robinson et al., 2007; Daneshvar et al., 2010; Aldekoa et al., 2015). Considering these variabilities requires streamflow and PPCPs emissions at the selected time scale, typically the daily or the monthly scale. Streamflow may be obtained from recorded data or from hydrological modeling. Similarly to GREAT-ER, all decay processes are lumped in a single first-order decay rate, and sorption by sediments is included through a linear equilibrium isotherm. Both the decay rate and the partition coefficient are temperature dependent through the Arrhenius law.

To summarize, we propose a new parsimonious, in terms of parameters, in-stream transport model which includes the concurrent effects of dilution, dispersion and decay of PPCPs in surface waters. Its strength is in the parametrization of the releases as a function of human resident population and touristic fluxes, the latter varying seasonally, both considered as a proxy of the sewage effluents. Human population and touristic fluxes data are widely available and this makes the model applicable in a variety of situations, despite the lack of systematic data on the contamination by PPCPs. Moreover, our model can be easily coupled to existing hydro-climatological models providing streamflow and water temperatures in the catchment of interest and is consistent with the general framework developed by Botter et al. (2011) under the hypothesis that <sup>[..<sup>32</sup>]</sup>transient flow can be represented as a superimposition of stationary flow fields.

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<sup>26</sup>removed: larger complexity of the model

<sup>27</sup>removed: Our model is parsimonious in terms of number of parameters, and requires streamflow and PPCPs emissions at the selected time scale, typically the daily scale. Streamflow may be obtained from recorded data or from hydrological modeling. Similarly to GREAT-ER all decay processes are lumped in a single first-order decay rate, and sorption by sediments is included through a linear equilibrium isotherm. Both the decay rate and the partition coefficient are temperature dependent through the Arrhenius law. Removing the stationary hypothesis is

<sup>28</sup>removed: transient conditions, due to variability in the consumption of PPCPs and streamflow,

<sup>29</sup>removed: non-stationarities

<sup>30</sup>removed: (Loraine and Pettigrove, 2006; Robinson et al., 2007; Daneshvar et al., 2010; Aldekoa et al., 2015) in both predicted concentrations and in the estimation of the

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The model is presented in Sect. [..<sup>33</sup> ]2, whereas Sect. [..<sup>34</sup> ]3 describes the Adige river basin and the data used for [..<sup>35</sup> ]illustrating model's application. Section 4 presents the inference of model parameters [..<sup>36</sup> ]and Sect. 5 discusses the simulations performed to estimate the seasonal loads [..<sup>37</sup> ]in the Adige catchment. Finally, a discussion of the main findings and the conclusions are presented in Sect. 6.

## 5 2 The Model

[..<sup>38</sup> ] The building block of our modeling approach is the solution of the one-dimensional Advection Dispersion Reaction Equation (ADRE) within a channel (stream) connecting two nodes of the river network (Bachmat and Bear, 1964):

$$(1 + K_d) \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} = \alpha_L v \frac{\partial^2 C}{\partial x^2} + r \quad (1)$$

where  $C$  [ $\text{ML}^{-3}$ ] is the solute concentration,  $x$  [ $\text{L}$ ] is the Lagrangian coordinate measured along the [..<sup>39</sup> ]channel,  $t$  [ $\text{T}$ ] is  
 10 time,  $v$  [ $\text{L T}^{-1}$ ] is the mean velocity,  $\alpha_L$  [ $\text{L}$ ] is the local dispersivity,  $K_d$  [ $-$ ] is the partition coefficient of the linear equilibrium isotherm representing sorption to the sediments, and  $r$  [ $\text{ML}^{-3} \text{T}^{-1}$ ] is the sink/source term representing the decay due to bio-geochemical reactions occurring in the liquid phase. The solute decays according to a first-order irreversible reaction  $r = -kC$ , where  $k$  [ $\text{T}^{-1}$ ] is the reaction rate lumping all the decay mechanisms occurring in the liquid phase. By introducing the following transformation:  $C(x, t) = \tilde{C}(x, t) e^{-kt}$ , Eq. (1) reduces to the classical Advection Dispersion Equation (ADE) in  
 15 the transformed concentration  $\tilde{C}$ :

$$(1 + K_d) \frac{\partial \tilde{C}}{\partial t} + v \frac{\partial \tilde{C}}{\partial x} = \alpha_L v \frac{\partial^2 \tilde{C}}{\partial x^2} \quad (2)$$

[..<sup>40</sup> ]The model (Eq. 1) assumes that the velocity is steady state, but it can be used to simulate representative states of a slowly varying flow approximated as the superimposition of a sequence of steady state velocity fields. This is acceptable if the characteristic time of water discharge variations is larger than the residence time [..<sup>41</sup> ]within the channel. Considering  
 20 the typical lengths of the channels composing a river network and the time scales at which the PPCPs loads are available, time variability can be captured at daily or larger time scales. However, also in steady state conditions water discharge,

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<sup>38</sup>removed: We model transport of a reactive solute along a stream of the river network by means of the following

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<sup>41</sup>removed: of the solute within the network, thereby excluding flooding events. This approximation can be applied also to estimate solute export at the monthly time scale with the velocity  $v$  in the Eq. (1) averaged at the monthly time-scale. In addition, we assume the velocity to vary spatially according to the

**Table 1.** Concentrations of the 5 selected pharmaceuticals recorded in surficial waters worldwide.

|                              |                             |                               |
|------------------------------|-----------------------------|-------------------------------|
| <b>Diclofenac</b>            |                             |                               |
| <i>Country</i>               | <i>Concentration [ng/l]</i> | <i>Reference</i>              |
| U.S.                         | 21 - 34                     | Mohapatra et al. (2016)       |
| Switzerland                  | 99                          | Tixier et al. (2003)          |
| Canada                       | 26 - 194                    | Metcalf et al. (2003)         |
| France                       | 290 - 410                   | Ferrari et al. (2004)         |
| Germany                      | 420 - 2100                  | Ferrari et al. (2004)         |
| Sweden                       | 10 - 120                    | Bendz et al. (2005)           |
| Spain                        | 0.25-280                    | Aldekoa et al. (2013)         |
| India                        | 1.41-41.3                   | Sharma et al. (2019)          |
| Malaysia                     | 1.11-4.92                   | Praveena et al. (2018)        |
| Northern Antarctic Peninsula | 7761                        | González-Alonso et al. (2017) |
| Spain                        | 89.53–176.78                | López-Serna et al. (2012)     |
| Mexico                       | 258–1398                    | Rivera-Jaimes et al. (2018)   |
| <b>Ketoprofen</b>            |                             |                               |
| <i>Country</i>               | <i>Concentration [ng/l]</i> | <i>Reference</i>              |
| Switzerland                  | 180                         | Tixier et al. (2003)          |
| Australia                    | <10                         | Scott et al. (2014)           |
| Canada                       | 12 - 50                     | Metcalf et al. (2003)         |
| Sweden                       | 10 - 70                     | Bendz et al. (2005)           |
| India                        | 2.71-107                    | Sharma et al. (2019)          |
| <b>Clarithromycin</b>        |                             |                               |
| <i>Country</i>               | <i>Concentration [ng/l]</i> | <i>Reference</i>              |
| U.S.                         | 48 - 66                     | Mohapatra et al. (2016)       |
| South Korea                  | 49 - 443                    | Kim et al. (2009)             |
| Italy                        | 8.3 - 20.3                  | Zuccato et al. (2005)         |
| Japan                        | 232                         | Arizono (2006)                |
| Germany                      | 210                         | Ternes et al. (2007)          |
| China                        | 9.9                         | Asghar et al. (2018)          |
| <b>Irbesartan</b>            |                             |                               |
| <i>Country</i>               | <i>Concentration [ng/l]</i> | <i>Reference</i>              |
| Slovene                      | 0.2 – 9.3                   | Klančar et al. (2018)         |
| China                        | 18                          | Asghar et al. (2018)          |
| <b>Sulfamethoxazole</b>      |                             |                               |
| <i>Country</i>               | <i>Concentration [ng/l]</i> | <i>Reference</i>              |
| U.S.                         | 313 - 342                   | Mohapatra et al. (2016)       |
| India                        | 357                         | Mohapatra et al. (2016)       |
| Australia                    | <5                          | Scott et al. (2014)           |
| France                       | 70 - 90                     | Ferrari et al. (2004)         |
| Germany                      | 480 - 2000                  | Ferrari et al. (2004)         |
| Sweden                       | 0 - 10                      | Bendz et al. (2005)           |
| Malaysia                     | 19.3 - 75.5                 | Praveena et al. (2018)        |
| China                        | 2.5                         | Asghar et al. (2018)          |

and therefore flow velocity, changes along the river network. The corresponding spatial variability can be captured by means of the following power law expression<sup>[..<sup>42</sup> ]</sup>:

$$v = \Phi(A) Q^{\Psi(A)} \quad (3)$$

<sup>[..<sup>43</sup> ]</sup>where  $Q$  is the water discharge. Equation (3) was proposed by Dodov and Foufoula-Georgiou (2004) for the velocity  $v_p$  <sup>[..<sup>44</sup> ]</sup>corresponding to the  $p$ -quantile,  $Q_p$  <sup>[..<sup>45</sup> ]</sup>, of the water discharge as a generalization of the following power law expression:  $v_p \propto Q_p^m$ , introduced in the pioneering work of Leopold and Maddock (1953), who noticed that the exponent  $m$  varies in dependence of the contributing area  $A$  [km<sup>2</sup>] <sup>[..<sup>46</sup> ]</sup>. In addition,  $\Phi$  and  $\Psi$  are <sup>[..<sup>47</sup> ]</sup>time-invariant scaling coefficients in agreement with the analysis of Dodov and Foufoula-Georgiou (2004) who showed that they are independent of the quantile chosen. The expressions of  $\Phi$  and  $\Psi$ , provided by Dodov and Foufoula-Georgiou (2004) <sup>[..<sup>48</sup> ]</sup>for a representative dataset of 85 gauging stations in Kansas and Oklahoma, are reproduced in the Appendix A. <sup>[..<sup>49</sup> ]</sup>

Equation (2) should be complemented with suitable initial and boundary conditions. The initial conditions are of zero concentration  $C(x, 0) = 0$  and zero absorbed concentration  $C^*(x, 0) = 0$  along the <sup>[..<sup>50</sup> ]</sup>channel. A suitable upstream boundary condition, mimicking the typical release condition at the WWTPs and industrial sewage systems is of continuous mass flux injection  $\dot{M}(t)$  [M T<sup>-1</sup>] at the position  $x_0$ . In addition, we assume that the <sup>[..<sup>51</sup> ]</sup>channel is semi-indefinite with the boundary condition <sup>[..<sup>52</sup> ]</sup>of zero flux concentration, <sup>[..<sup>53</sup> ]</sup> $C_F(x, t) = \tilde{C}(x, t) - \alpha_L \partial \tilde{C}(x, t) / \partial x = 0$  <sup>[..<sup>54</sup> ]</sup>at  $x \rightarrow \infty$ . This condition is equivalent to assuming that the downstream boundary condition does not affect mass flux.

Owing to the linearity of Eq. (2), the flux concentration  $C_F$  of the solute at a given position  $x$  along the <sup>[..<sup>55</sup> ]</sup>channel assumes the following expression:

$$C_F(x, t) = \int_0^t C_{F,in}(t_0) g_M(x, t - t_0) dt_0 \quad (4)$$

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<sup>42</sup>removed: proposed by Dodov and Foufoula-Georgiou (2004)

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<sup>44</sup>removed: , as a function of the same quantile of water discharge

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<sup>47</sup>removed: scaling coefficients, which do not depend on the chosen quantile

<sup>48</sup>removed: , by using a

<sup>49</sup>removed: The expression (3) is a generalization of the power law expression  $v \propto Q^m$  introduced in the pioneering work of Leopold and Maddock (1953), 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 therefore assume the velocity spatially uniform within the channels.

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where  $C_{F,in} = \dot{M}(t)/Q(t)$  is the flux concentration at the injection point  $x = x_0$ , under the assumption that the release mass rate is  $\dot{M}$  and that mixing with stream water occurs instantaneously. In Eq. (4) the transfer function assumes the following form:

$$g_M(x, t) = g(x, t) e^{-k t} \quad (5)$$

5 with

$$g(x, t) = \frac{x - x_0}{\sqrt{4\pi\alpha_L v_R t^3}} \exp \left\{ -\frac{[x - x_0 - v_R t]^2}{4\alpha_L v_R t} \right\} \quad (6)$$

being the solution of the Eq. (2) for an instantaneous mass injection such that:

$$c_F(x_0, t) = \delta(t) \quad (7)$$

where  $c_F = \dot{M}/M = C_{F,in}/(M/Q)$   $[T^{-1}]$  is the flux concentration for a unit ratio between the total injected mass and water discharge and  $\delta(\cdot)$   $[T^{-1}]$  is the Dirac delta function. Equation (6) is the classical solution discussed in Kreft and Zuber (1978, Eq. 11) for both injection and detection in flux and unitary ratio  $M/Q$ .

## 2.1 Extension to the river network

Let us consider the generic network represented in Fig. (1). <sup>56</sup>For an injection occurring at the position  $x_{0,i}$  along the channel number  $i$  <sup>57</sup>the solute follows this path:

$$(i, 1) \rightarrow (i, 2) \rightarrow (i, 3) \rightarrow \dots (i, j) \rightarrow \dots (i, n_i) \quad (8)$$

where  $(i, j)$  indicates the  $j$ -th channel in the ordered sequence of channels connecting the injection point to the control section  $CS$ , and  $n_i$  is the total number of elements <sup>58</sup>in the sequence. In the presence of lakes and reservoirs corresponding elements should be added to the ordered sequence. The input signal at  $x = x_{0,i}$  is transferred to the end of the channel  $i \equiv (i, 1)$  by means of the expression (4), which can be rewritten as follows:

$$C_F(L_{(i,1)}, t) = C_{F,in}^{(i)}(t) * g_M(L_{(i,1)} - x_{0,i}, t) \quad (9)$$

where  $C_{F,in}^{(i)}$  is the concentration flux of the solute released at the coordinate  $x_{0,i}$  along the channel  $i$  of length  $L_{(i,1)}$  and  $*$  indicates the convolution integral of Eq. (4).

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The signal arriving from the channel  $(i, 1)$  is [..<sup>59</sup>] first modified to take into account the [..<sup>60</sup>] effect of dilution of merging channel(s) (i.e. the channel  $l$  in the Fig. [..<sup>61</sup>] 1) and then is propagated to the end of the following channel (i.e. the channel  $(i, 2)$ ). The same procedure is repeated for all the channels composing the path from the source to the control section. At the  $j$ -th channel in the sequence the convolution assumes the following form:

$$5 \quad C_F(L_{(i,j)}, t) = \left\{ \frac{Q_{(i,j-1)}(t)}{Q_{(i,j)}(t)} C_F(L_{(i,j-1)}, t) \right\} * g_M(L_{(i,j)}, t); \quad j = 2, \dots, n_i \quad (10)$$

For the element lake or reservoir a similar expression can be written with  $g_M(L_{(i,j)}, t)$  replaced by the function  $g_M(s_k, t)$ , representing the residence time distribution within this element (here  $s_k$  identifies the storage element encountered along the path). For simplicity, in the following with the term lake we will indicate both natural lakes and reservoirs. Finally, owing to linearity of the transport processes, the flux concentrations  $C_F(L_{(i,n_i)})$ ,  $i = 1, \dots, N$ , propagated from the  $N$  sources within  
10 the catchment are summed up to obtain the total concentration flux at the control section  $CS$ :

$$C_{F,S}(t) = \sum_{i=1}^N C_F(L_{(i,n_i)}, t) \quad (11)$$

Under the additional assumption that  $\frac{Q_{(i,j-1)}(t)}{Q_{(i,j)}(t)} \simeq \frac{A_{(i,j-1)}}{A_{(i,j)}}$ , where  $A_{(i,j)}$  is the contributing area to the  $j$ -th channel, the sequence of convolutions assumes the following form:

$$C_F(L_{(i,n_i)}, t) = \frac{A_{(i,1)}}{A_{(i,n_i)}} g_M(L_{(i,1)} - x_{0,i}, t) * g_M(L_{(i,2)}, t) * \dots * g_M(L_{(i,n_i)}, t) * g_M(s_1, t) * \dots * g_M(s_{n_s}, t) * C_{F,in}^{(i)}(t) \quad (12)$$

15 with  $A_{(i,n_i)} = A_S$ , the contributing area at the control section [..<sup>62</sup>], and  $s_k$ ,  $k = 1, \dots, n_s$ , identifies the  $k$ -th of  $n_s$  lake elements belonging to the path. The pdf of the lake element depends on the nature of mixing occurring in the lake and varies between an exponential pdf, in case of full mixing, and a Dirac delta distribution, in case of plug flow (Botter et al., 2011).

At the release point  $x_{0,i}$  the flux concentration can be expressed as follows:  $C_{F,in}^{(i)}(t) = \frac{\dot{M}_i(t)}{Q_{(i,1)}(t)}$ , with  $\dot{M}$  indicating the released mass flux from the WWTP and  $Q_{(i,1)} = Q_i$  is the stream water discharge at the point of release.

20 The released mass flux from the  $i$ -th WWTP is given by the product of the unitary released mass flux (i.e. the mass flux released per person)  $\gamma_i$  [M T<sup>-1</sup>] and the population  $P_i(t)$  served by the WWTP:  $\dot{M}_i(t) = \gamma_i P_i(t)$ .

The unitary mass flux is given by:

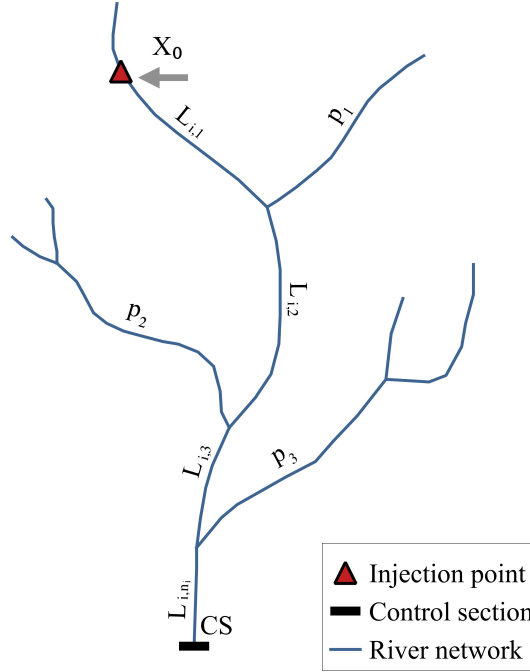
$$\gamma_i = \frac{\alpha_i D_i \beta_i (1 - f_i)}{\Delta T} \quad (13)$$

<sup>59</sup>removed: propagated to the end of the following channel (i.e. the channel  $(i, 2)$ ) taking

<sup>60</sup>removed: dilution occurring at the node as an effect of the joining

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**Figure 1.** Sketch of the network with indicated the labeling of the streams, a release point at the Lagrangian coordinate  $x_{0,i}$  along the  $i$ -th stream, and the control section (CS). The distance between the  $i$ -th release and the Control Section is defined as  $\sum_{j=1}^{n_i} L_{i,j}$ . Along this path, tributaries ( $p_1, p_2$  and  $p_3$  in figure) contribute with further water discharge, thereby causing dilution.

where  $\alpha_i [-]$  is the assimilation factor, corresponding to the fraction of daily dose  $D_i [\text{M T}^{-1}]$  per person that is released by the human body,  $\beta_i [-]$  is the percentage of usage of the targeted active principle,  $f_i < 1$  is the decay factor of the WWTP and  $\Delta T$  is the transformation factor of time to make the units congruent with the time step used in the model.

Notice that the model is based on a segmentation of the path from the source to the control section. Therefore, diffused contributions can be evaluated at the level of the sub-catchment and treated as a point source located at the middle of the channel draining the sub-catchment. The length of the channels composing the river network, and therefore the size of the sub-catchments can be varied according to the threshold in the contributing area chosen during the identification of the river network from the Digital Terrain Model (see e.g. Rodriguez-Iturbe and Rinaldo, 1997). Hence, the maximum detail with which the spatial variability of the diffused contribution is reproduced can be controlled by the modeler simply by changing the density of the network. Notice that this has also an effect on the minimum time scale at which variability of the flow field can be captured, through the control of the channel length on the residence time. In this study, sources of

diffused origin are not relevant since the region uses separate sewer systems, which eliminate sewer's overflow and the possible input from manure cannot be evaluated with the information available.

The classical study by Rinaldo et al. (1991) showed that geomorphological dispersion acting at the network scale overwhelms local dispersion in shaping the hydrological response of a catchment. The same assumption, preventively verified numerically, can be introduced in our model in which dilution caused by the progressive increase of water discharge as the solute moves downstream rapidly overwhelms dilution due to local dispersion [acting at the level of the channel](#), which can be neglected by assuming  $\alpha_L \rightarrow 0$ . Under this condition the transfer function of the channel (i.e. Eq. [\[.63\]](#) 5), with  $g$  provided by Eq. (6), reduces to:

$$g_M(x, t - t_0) = \delta[x - x_0 - v_R(t - t_0)] \exp[-k(t - t_0)] \quad (14)$$

- 10 where  $\delta[T^{-1}]$  is the Dirac Delta distribution. Neglecting  $\alpha_L$  has the advantage of reducing by one the number of parameters that should be inferred from the data, thereby reducing the risk of over-parameterization, when, as often occurs, concentration data are scarce. [\[.64\]](#) [In the absence of lakes the](#) substitution of Eq. (14) into Eq. (12) leads, to the following expression of the flux concentration:

$$C_F(L_{(i,n_i)}, t) = \frac{A_{(i,1)}}{A_{(i,n_i)}} C_{F,in}^{(i)} \left( t - \sum_{j=1}^{n_i} \tau_{i,j} \right) \exp \left[ -k \sum_{j=1}^{n_i} \tau_{i,j} \right] \quad (15)$$

- 15 [\[.65\]](#) [If a lake is encountered along the path and its functioning can be represented as a plug-flow such that](#)  $g_M(s_k, t) = \delta(t - \tau_{s_k})$ , Eq. (15) should be generalized by adding the residence time  $\tau_{s_k}$  (and that of the other lakes encountered along the path) to the channels residence times  $\tau_{i,j}$ . If the hypothesis of plug-flow does not hold, the pdfs of all the lakes encountered along the path should be convoluted to the Eq. (15).

[The](#) travel time  $\tau_{i,j}$  of the  $i$ -th channel [\[.66\]](#) [along](#) the path (i.e. Eq. [\[.67\]](#) 8) assumes the following expression:

$$20 \quad \tau_{i,j} = \frac{L_{(i,j)} - \delta_{1j} x_{0,i}}{v_{0,R}(A_{(i,j)})} \quad (16)$$

where the retarded velocity is given by

$$v_{0,R}(A_{(i,j)}) = \frac{1}{1 + K_d} \Phi(A_{(i,j)}) (q A_{(i,j)})^{\Psi(A_{(i,j)})} \quad (17)$$

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In Eq. (17),  $q$  [ $\text{L T}^{-1}$ ] is the specific water discharge (i.e. the water discharge per unit contributing area [<sup>68</sup>] is considered constant through the catchment). In Eq. (16)  $\delta_{1j}$  is the Kronecker delta, which is equal to 1 when  $j = 1$  and zero otherwise.

Finally, according to the Arrhenius law, the coefficient of decay  $k$  assumes the following expression (Arrhenius, 1889):

$$k = A \exp \left[ -\frac{E_A}{\mathcal{R} \theta} \right] \quad (18)$$

- 5 where  $A$  [ $\text{s}^{-1}$ ] is the frequency factor,  $E_A$  [ $\text{kJ mol}^{-1}$ ] is the activation energy,  $\mathcal{R} = 8.314 * 10^{-3}$   $\text{kJ K}^{-1} \text{mol}^{-1}$  is the gas constant and  $\theta$  [K] is the water temperature. Notice that  $v_{0,R}$  changes along the river network according to the contributing area.

### 3 Materials and methods

#### 3.1 The Adige river basin

- 10 We applied our model to the Adige, a large Alpine river in the North-Eastern Italy, with the parameters inferred by means of inverse modeling applied to one of its main tributaries: the Noce river. The Adige catchment area is of 12,100  $\text{km}^2$  (Fig. 2) with the large majority of the basin (91%) belonging to the Trentino-Alto Adige region. The main stem has a length of 409 km from the spring to the estuary in the Adriatic sea. Along its course the river receives the contributions of Passirio, Isarco, Rienza, Noce, Avisio, Fersina and Leno[<sup>69</sup>]. Streamflow is characterized by a first maximum in spring, due to snowmelting,
- 15 and a second one in autumn caused by cyclonic storms. Climate is typically Alpine and characterized by dry winters, snow and glacier-melt in spring, and humid summers and autumns (Lutz et al., 2016). The Noce [<sup>70</sup>] rises from the reliefs of the Ortles-Cevedale and Adamello-Presanella groups and flows first to East, then around its middle course it turns to South-East and enters the Adige river close to the town of Mezzolombardo, North of the city of Trento (Fig. 2). Its total contributing area is of 1,367  $\text{km}^2$  and [<sup>71</sup>]the main stem is 82 km long (Majone et al., 2016).
- 20 The Noce river is exploited for hydropower production with 4 reservoirs, two in the upper course (Careser and Pian Palù) and two in the middle course (S. Giustina and Mollaro). Careser and Pian Palù are in headwaters with no WWTPs upstream and therefore they enter in the model only with their effect on the water discharge. The other two are downstream of a few WWTPs (see Fig. 2 and Table B1 in the Appendix B) and therefore their effect on the residence time should be included. The Mollaro reservoir is just downstream of the S. Giustina reservoir and since no release points are
- 25 in between we merged them in a single equivalent reservoir. A recent publication of the Hydrological Observatory of the Province of Trento (2007) shows that in the period 2001-2005 the average volume stored in the S. Giustina reservoir was of  $12.089 \times 10^6$   $\text{m}^3$ . In the same period the mean water discharge was  $25.8 \text{ m}^3 \text{s}^{-1}$ , thereby leading to a mean residence time of  $\tau_{s_1} = \bar{V}/\bar{Q} = 53.7$  days. Mollaro has a little storage volume compared to that of S. Giustina. At the maximum

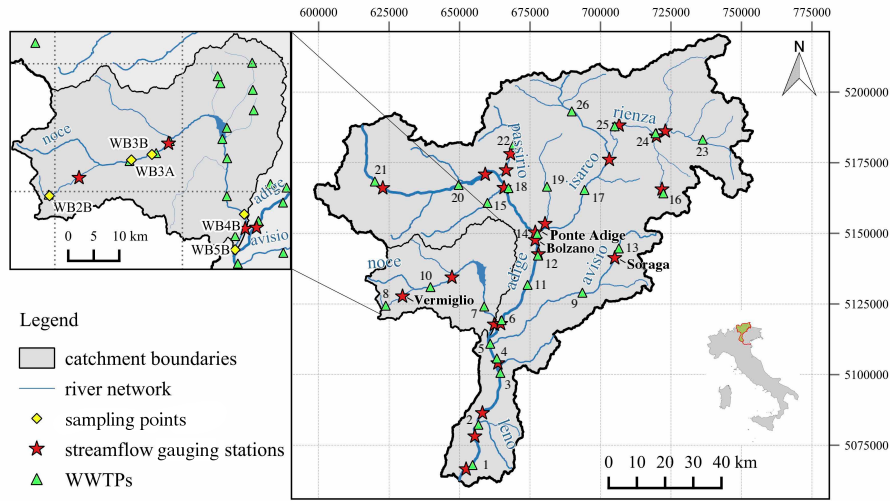
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<sup>68</sup>removed: here

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<sup>70</sup>removed: river is a tributary of the Adige river. It

<sup>71</sup>removed: its total length is of



**Figure 2.** Map of the Adige river basin and its main tributaries with a zoom on the Noce river basin (upper left panel). Green triangles represent the main WWTPs whereas red stars indicate the gauging stations. The gauging stations used as control sections are identified with their names (i.e. Soraga, Vermiglio, Ponte Adige and Bronzolo). Only for the Noce basin, yellow diamonds shows the sampled locations during the two sampling campaigns of February and July, 2015.

storage (i.e.  $0.860 \times 10^6 \text{ m}^3$ ) the mean residence time is of  $\tau_{s_2} = 0.38$  days, which summed to the mean residence time of S. Giustina leads to a total residence time of the two reservoirs of  $\tau_s = \tau_{s_1} + \tau_{s_2} = 54$  days. Notice that the storage of Mollaro has been considered constant because of its small volume which allows very little flexibility for storing the water released from the S. Giustina reservoir (the S. Giustina reservoir feeds the Taio power plant which release point is just upstream of the Mollaro reservoir) and counts only for a small fraction of the total residence time of the two reservoirs. In this situation the water coming from S. Giustina and the small catchment between the two reservoirs is stored for a very short time in the Mollaro reservoir with respect to the residence time of S. Giustina, such that fluctuations of its storage volume are not influencing significantly  $\tau_s$ .

### 3.2 Meteorological, hydrological and chemical data

- Stream water of the Noce was sampled in two sampling campaigns performed respectively on February 15-17, 2015 and July 3-5, 2015 at the following sites (see Fig. 2): Tonale pass, immediately downstream of the WWTP serving a large ski area (WB2B), two sites in Mezzana, immediately downstream of the WWTP serving the middle [..<sup>72</sup>] Sole valley (WB3A and WB3B) and in two sites in the town of Mezzocorona, lower Non valley, immediately upstream and downstream of the restitution of the Mezzocorona power plant (WB4B and WB5B[..<sup>73</sup>]), respectively. The Mezzocorona power plant is fed by the water of the Mollaro reservoir (see Sect. 3). Details on sampling procedures, sampling locations, and analyses performed

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**Table 2.** Streamflow [l/s] and water temperature [°C] data of the 5 selected sampling sites during the two sampling campaigns.

| <i>Sampling sites</i> | <b>February</b>          |                               | <b>July</b>              |                               |
|-----------------------|--------------------------|-------------------------------|--------------------------|-------------------------------|
|                       | <i>stream flow [l/s]</i> | <i>water temperature [°C]</i> | <i>stream flow [l/s]</i> | <i>water temperature [°C]</i> |
| WB2B                  | 85                       | 3.4                           | 610                      | 12.6                          |
| WB3A                  | 3366                     | 3.6                           | 13579                    | 9.8                           |
| WB3B                  | 3602                     | 5.3                           | 14529                    | 13.1                          |
| WB4B                  | 35742                    | 7.7                           | 28476                    | 14.8                          |
| WB5B                  | 36752                    | 5.4                           | 29281                    | 13.7                          |

are provided in the work by Mandaric et al. (2017). Table 2 reports streamflow and water temperature data measured during the two campaigns at the five sampling sites. Notice that both campaigns were performed in dry conditions (i.e. absence of precipitation during the samplings). These two periods were selected such as to capture extreme conditions in the catchment. Winter is the main touristic season with a large number of tourists hosted in hotels and houses in the ski area and along the Sole valley, while streamflow is at the annual minimum. On the other hand, summer is characterized by lower, yet significant, touristic presences and high streamflow due to snow melting. In the winter campaign, 36 out of the 80 investigated pharmaceuticals were detected in water samples with concentrations above their respective Limit Of Quantification (LOQ) whereas in the summer campaign, this number reduced to 15, and with concentrations mostly lower than in winter (Mandaric et al., 2017). The quality of the measurements utilized in the present work is granted by the protocols used in the sampling campaign, the care in maintaining and shipping the samples, and the analytical methodologies used in the laboratory. For further details on the protocols followed in sampling, handling, shipping and analyzing the samples, we refer to the previous work of (Mandaric et al., 2017).

Among the detected pharmaceuticals, the five with the highest concentrations in both sampling campaign were selected for simulation. They are:

- 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;
- Irbesartan: nonpeptide angiotensin II antagonist with antihypertensive activity.

Although detected only in February, diclofenac was included because it belongs to the watch list in the directive 2013/39/EU of the European Parliament. For additional information on these compounds we refer to the PubChem Compound database [..<sup>74</sup> ][..<sup>75</sup> ](PubChem).

The locations of WWTPs were obtained from the local authorities responsible for urban waste water treatment in the provinces of Trento [..<sup>76</sup> ][..<sup>77</sup> ](ADEP) for Trentino Province and Bolzano [..<sup>78</sup> ][..<sup>79</sup> ](APPA, b) for Alto Adige Province. The geometry of the river network, including the distances of the WWTPs from the control sections, were obtained from the official river network shape file, which includes deviation of the natural river courses [..<sup>80</sup> ][..<sup>81</sup> ][..<sup>82</sup> ](EEA, 2017; ISPRA, 2015). All the spatial analyses were performed through [..<sup>83</sup> ][..<sup>84</sup> ]the software QGIS (QGIS, 2018). Resident population and touristic presences were obtained from the census offices of Trento [..<sup>85</sup> ][..<sup>86</sup> ][..<sup>87</sup> ](ISPAT) and Bolzano (ASTAT) at annual and monthly resolution, respectively. Only for the Noce sub-catchment the touristic presences were also available at the sampling days. Population was assigned to the WWTPs according to the served municipalities and resident population was assumed constant through the year. Daily streamflow time series (Q) were obtained from the hydrological offices of the Provinces of Trento [..<sup>88</sup> ][..<sup>89</sup> ][..<sup>90</sup> ](Ufficio-Dighe) and Bolzano (Ufficio-Idrografico). Monthly streamflow time series at the gauging stations were then computed by aggregating daily values. Finally, water temperatures (WT) at the streamflow gauging stations were provided by the Environmental Protection Agencies of the provinces of Trento [..<sup>91</sup> ][..<sup>92</sup> ][..<sup>93</sup> ](APPA, a) and Bolzano (APPA, b) at monthly resolution (Fig. 2). The parameters  $\alpha_i$ ,  $\beta_i$  and  $D_i$  of Eq. (13) are obtained from the datasets of the Collaborating Centre for Drug Statistics Methodology of the World Health Organization [..<sup>94</sup> ][..<sup>95</sup> ](WHO) and the Italian Agency of Drug [..<sup>96</sup> ][..<sup>97</sup> ](AIFA).

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### 3.3 [..<sup>98</sup>]

#### 4 Inference of the model parameters

Concentrations along the river network were predicted by an adaptation of Eq. (15) to include the effect of the S. Giustina and Mollaro Reservoirs. In the absence of information supporting a more accurate mixing model, we assumed that the concentration within the equivalent reservoir simulating the effect of both reservoirs, is the total load entering in the  $\tau_s = 54$  days before the simulation day (see Sect. 3 for the computation of  $\tau_s$ ) divided by the mean volume of the two reservoirs evaluated in the same period. Given that the load is parametrized by the amount of population and that the fluctuating touristic presences is known only at the monthly scale, we assigned the average monthly load to each day of the month. According to Eq. (15) the load entering the equivalent reservoir is computed by reducing the mass released from the upstream WWTPs by the factor  $\exp \left[ -k \left( \sum_{j=1}^{n_i} \tau_{i,j} + \bar{\tau}_s \right) \right]$ , where  $\bar{\tau}_s$  is the weighted residence time with respect to the population. Here we utilized  $\bar{\tau}_s$ , instead of  $\tau_s$ , in order to take into account that at a given day the mass with age  $\tau_a \in [0, \tau_s = 54 \text{ days}]$  contained into the reservoir depends on the number of persons within the catchment  $\tau_a$  days before. In other words, the age distribution of solute particles contained into a volume of water sampled at the outlet of the lake is proportional to the temporal distribution of the population of the catchment in the  $\tau_s$  days before. Notice that  $\tau_{i,j}$  is in any case smaller than 1 day.

To comply with Occam's razor principle (MacKay, 2003, ch. 28), suggesting parsimony in selecting model complexity and considering the very limited amount of concentration data available, [..<sup>99</sup>] the parameters in the Eq. (13) are assumed the same for all the WWTPs and [..<sup>100</sup>] since  $\gamma$  is inferred the abatement  $f$  is assumed to be zero. This simplification is supported by the fact that all WWTPs of each of the two provinces are managed by the same agency by using similar technologies. The parameters space has been explored by Latin Hypercube sampling with the probability distribution assumed multi-log-normal with means and variances of  $\gamma$  and  $k$  provided in Table 3 and obtained from the pharmacological databases described in Sect.

3.2. [..<sup>101</sup>] [..<sup>102</sup>] [..<sup>103</sup>] [..<sup>104</sup>] [..<sup>105</sup>] [..<sup>106</sup>] [..<sup>107</sup>] [..<sup>108</sup>] [..<sup>109</sup>] [..<sup>110</sup>]

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<sup>98</sup>removed: Inference of the model parameters

<sup>99</sup>removed: we assume that

<sup>100</sup>removed: that the abatement is zero (i. e.  $f_i = 0$ ,  $i = 1, \dots$ ). Hence, under these conditions  $\gamma_i = \gamma$

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<sup>102</sup>removed: Means ( $\bar{\gamma}$ ) and variances ( $\sigma^2$ ) of the log-normal distributions of the unitary mass fluxes ( $\gamma$ ) and of the coefficients of decay ( $\bar{k}$ ) for the 5 selected pharmaceuticals. The standard deviation of the associated normal distributions, with unitary means, was set equal to 3 in order to explore several order of magnitudes and, hence, all the possible physical values.

<sup>103</sup>removed:  $\bar{\gamma}$

<sup>104</sup>removed:  $\sigma_{\gamma}^2$

<sup>105</sup>removed:  $\bar{k}$

<sup>106</sup>removed:  $\sigma_k^2 [\text{s}^{-2}]$

<sup>107</sup>removed:  $1.37E + 14$

<sup>108</sup>removed:  $1.23E + 03$

<sup>109</sup>removed:  $7.82E + 13$

<sup>110</sup>removed:  $1.31E + 03$

[..<sup>111</sup>][..<sup>112</sup>]

[..<sup>113</sup>][..<sup>114</sup>]

[..<sup>115</sup>][..<sup>116</sup>]

5 The inference of model's parameters was performed by using concentration measurements along the Noce river as observational variables. The unitary mass flux release  $\gamma$  may change seasonally as an effect of variability in drugs consumption, due to changes in touristic fluxes, while the variability of  $k$  is reproduced through the Arrhenius law (Eq. [<sup>117</sup>]<sup>18</sup>). Four candidate models with different numbers of parameters (i.e.  $n_p$ ) are investigated:

- M1: a single value of  $\gamma$  is considered through the year and decay  $k$  is set to zero; this is a single parameter model ( $n_p = 1$ );
- 10 - M2: two values of  $\gamma$  are considered, one for the winter season and the other for the summer season,  $k = 0$  as for M1; therefore  $n_p = 2$ ;
- M3: a single value of  $\gamma$  is considered, as in M1, while decay is assumed to vary with temperature according to the Arrhenius law (Eq. [<sup>118</sup>]<sup>18</sup>). This model requires  $n_p = 3$  parameters, given that the Arrhenius law depends on  $A$  and  $E_A$ ;
- 15 - M4:  $\gamma$  varying seasonally as in M2 and  $k$  as in M3; therefore  $n_p = 4$ .

Since water temperature can be safely assumed constant in each sampling campaign, with the models M3 and M4 the inversion was performed by considering two values of  $k$ , one for the winter and one for the summer seasons, as [<sup>119</sup>]<sup>unknowns</sup> instead of  $A$  and  $E_A$ , successively the inferred values were used in Eq. (18), together with the water temperature, to compute the parameters  $A$  and  $E_A$  of the Arrhenius law.

20 The inference was performed for each of the four selected models by searching the parameters hyperspace through the Latin Hypercube Sampling (LHS) procedure (McKay et al., 1979) with the objective to identify the set of parameters that minimizes the following weighted least-squares criterion (see e.g., Carrera and Neuman, 1986; McLaughlin and Townley, 1996; Tarantola, 2005):

$$L(a) = [z - \mathcal{F}(a)]^T C_v^{-1} [z - \mathcal{F}(a)] + [\bar{a} - a]^T C_a^{-1} [\bar{a} - a] \quad (19)$$

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<sup>111</sup>removed:  $5.90E + 14$

<sup>112</sup>removed:  $2.13E + 05$

<sup>113</sup>removed:  $5.39E + 13$

<sup>114</sup>removed:  $5.60E + 03$

<sup>115</sup>removed:  $2.77E + 13$

<sup>116</sup>removed:  $2.90E + 03$

<sup>117</sup>removed: (18)). We investigated four possible

<sup>118</sup>removed: (18)

<sup>119</sup>removed: unknown

**Table 3.** Means ( $\bar{\gamma}$ ,  $\bar{k}$ ) and variances ( $\sigma_{\gamma}^2$ ,  $\sigma_k^2$ ) of the log-normal distributions of the unitary mass fluxes ( $\gamma$ ) and of the coefficients of decay ( $k$ ) for the 5 selected pharmaceuticals. The standard deviation of the associated normal distributions, with unitary means, was set equal to 3 in order to explore several order of magnitudes and, hence, all the plausible physical values.

| <i>Pharmaceutical</i>   | $\bar{\gamma}$ [ng hab <sup>-1</sup> d <sup>-1</sup> ] | $\sigma_{\gamma}^2$ [ng <sup>2</sup> hab <sup>-2</sup> d <sup>-2</sup> ] | $\bar{k}$ [s <sup>-1</sup> ] | $\sigma_k^2$ [s <sup>-2</sup> ] |
|-------------------------|--|--|------------------------------|---------------------------------|
| <b>Diclofenac</b>       | 2.09E + 06   | 1.37E + 14   | 1.87E − 05                   | 1.23E + 03                      |
| <b>Ketoprofen</b>       | 1.19E + 06   | 7.82E + 13   | 2.00E − 05                   | 1.31E + 03                      |
| <b>Clarithromycin</b>   | 8.98E + 06   | 5.90E + 14   | 3.25E − 03                   | 2.13E + 05                      |
| <b>Irbesartan</b>       | 8.20E + 05   | 5.39E + 13   | 8.53E − 05                   | 5.60E + 03                      |
| <b>Sulfamethoxazole</b> | 4.21E + 05   | 2.77E + 13   | 4.42E − 05                   | 2.90E + 03                      |

where  $a$  is the vector of the unknown model parameters,  $z$  is the vector containing the observational data,  $\mathcal{F}$  is the [\[..<sup>120</sup>\]](#)output of the model at the measurement points (i.e. [\[..<sup>121</sup>\]](#)the Eq. 15 modified as discussed above),  $C_v$  is the diagonal matrix of the error variances,  $C_a$  is a diagonal matrix which epitomizes the effect of uncertainty associated to the prior information, and  $\bar{a}$  is the vector of the prior estimates of the model's parameters (i.e. the means reported in Table 3). In addition, the superscript

5  $T$  indicates the transpose of the vector. Under the commonly assumed hypothesis that the model's errors ( $z - \mathcal{F}(a)$ ) and the residuals ( $\bar{a} - a$ ) are both normally distributed and independent, the minimum of the function (Eq. [\[..<sup>122</sup>\]](#)19) coincides with the Maximum of the A-Posteriori (MAP) probability distribution (McLaughlin and Townley, 1996; Rubin, 2003; Castagna and Bellin, 2009).

LHS was performed by dividing the parameters axes in  $N_L$  intervals of constant probability  $1/N_L$ , thereby resulting in a

10 partition of the hypercube in  $M = N_L^{n_p}$  cells. The upper [\[..<sup>123</sup>\]](#)boundary of the cell along the axis  $a_j$ ,  $j = 1, \dots, n_p$  of the hypercube is obtained by inverting the [\[..<sup>124</sup>\]](#)cumulative log-normal probability [\[..<sup>125</sup>\]](#)distribution:

$$P(a_j) = \int_0^{a_j} \frac{1}{\ln a_j \sqrt{2\pi\sigma_{y_j}^2}} \exp \left[ -\frac{(\ln a_j - \bar{y}_j)^2}{2\pi\sigma_{y_j}^2} \right] da_j \quad (20)$$

<sup>120</sup>removed: estimate of the observational data provided by the model

<sup>121</sup>removed: Eq. (15 ))

<sup>122</sup>removed: (19)

<sup>123</sup>removed: limit of the cells

<sup>124</sup>removed: cumulate of the

<sup>125</sup>removed: density function

at the following discrete values:  $\{1/N_L, 2/N_L, \dots, (N_L - 1)/N_L, 1\}$ . In Eq. (20) the first two moments assume the following expressions:

$$\bar{y}_j = \ln \left[ \frac{\bar{a}_j^2}{\sqrt{\bar{a}_j^2 + C_{a,jj}}} \right], \quad \text{and} \quad \sigma_{y_j}^2 = \ln \left[ 1 + \frac{C_{a,jj}}{\bar{a}_j^2} \right] \quad (21)$$

- where  $C_{a,jj}$  is the  $j$ -th diagonal term of the matrix  $C_a$ . A sampling point is then generated randomly within each cell, thereby obtaining a total number of  $M$  sampling points distributed within the hypercube. The sampling point that minimizes the function  $L(a)$  given by Eq. (19) is recorded together with its value and the procedure is repeated  $MC$  times, each time with a different random location within the cells. Inference is performed for each model with  $M = 100$  and  $MC = 10,000$ . Parameters inference was repeated by using the Nash-Sutcliffe Efficiency Index (NSE; Nash and Sutcliffe, 1970) as the objective function (this time by maximizing  $NSE$ ), obtaining optimal sets of parameters close to those identified by MAP.

The choice among the four models, each one with the optimal parameter set, has been performed by using the Akaike's information criterion (AIC; Akaike, 1974), which penalizes models with more parameters (Akaike, 1987):

$$AIC = p \ln \left( \frac{[z - \mathcal{F}(a)]^T [z - \mathcal{F}(a)]}{p} \right) + 2n_p \quad (22)$$

where  $p$  is the number of experimental data points and  $n_p$  is the number of parameters.

- The highest AIC values are obtained with the model M4 (217, on average for the 5 pharmaceuticals), which is then discarded. For this model the better fit granted by the larger number of parameters is not enough to justify higher model complexity, according to the Akaike criterion. Also the less complex model (i.e. M1) was discarded because of the poorer fit of the observations (AIC=206) with respect to models M2 and M3, both with a AIC approximately equal to 200. Given the importance of including seasonality in modeling bio-geochemical processes, the model

<sup>126</sup>removed: The

<sup>127</sup>removed: was also used

<sup>128</sup>removed: to maximize

<sup>129</sup>removed: obtained with

<sup>130</sup>removed: according to MAP criterium

<sup>131</sup>removed:  $N$

<sup>132</sup>removed: model

<sup>133</sup>removed: provided the highest values of AIC

<sup>134</sup>removed: and was therefore discarded. In this case

<sup>135</sup>removed: provided by the four parameters of the model

<sup>136</sup>removed: a

<sup>137</sup>removed: fitting

<sup>138</sup>removed: Considering

<sup>139</sup>removed: the

<sup>140</sup>removed: decay as attenuation factor, we selected

**Table 4.** Model M3 theoretical load coefficients ( $\gamma$ ), coefficients of decay ( $k_{february}$  and  $k_{july}$ ) and  $L$ -values for the 5 pharmaceuticals.

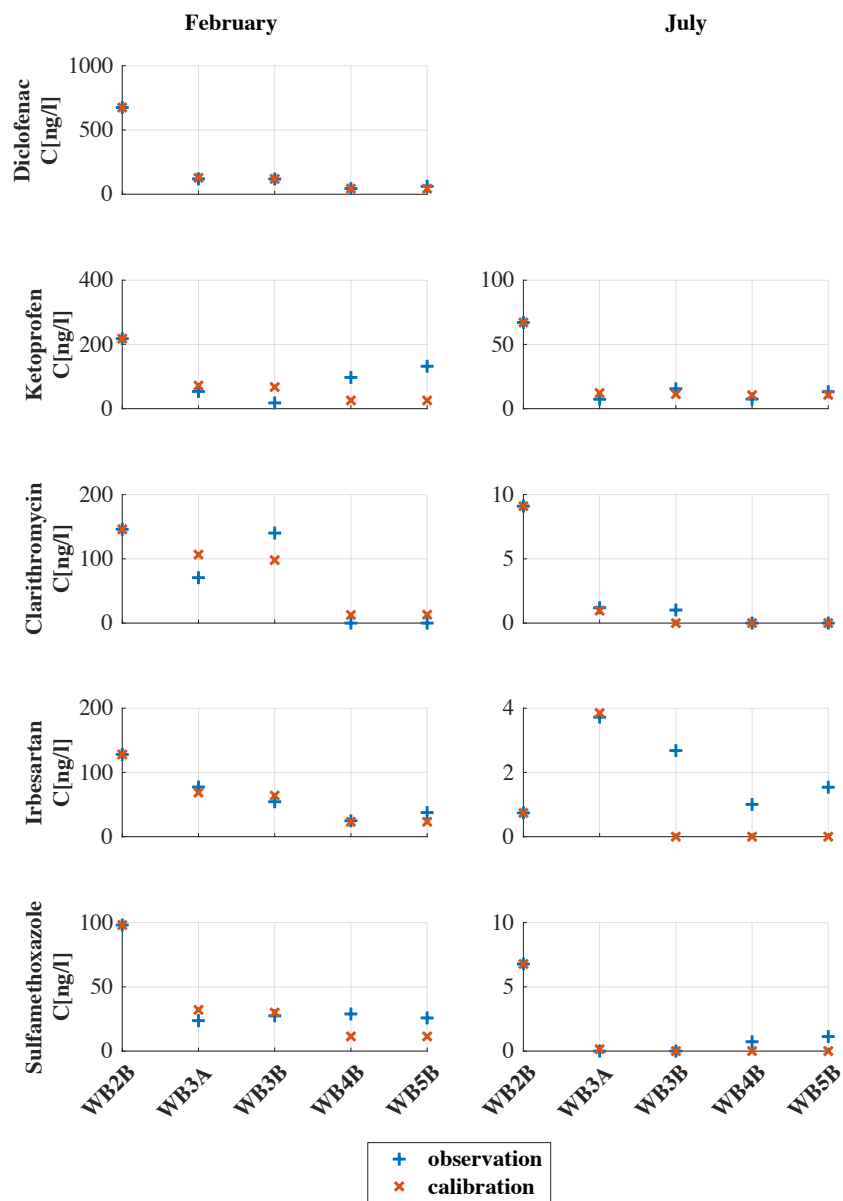
| <i>Pharmaceutical</i>   | $\gamma$ [ng hab <sup>-1</sup> d <sup>-1</sup> ] | $k_{february}$ [s <sup>-1</sup> ] | $k_{july}$ [s <sup>-1</sup> ] | $L$ [-] |
|-------------------------|--|-----------------------------------|-------------------------------|---------|
| <b>Diclofenac</b>       | 2.07E + 06                                       | 1.33E - 10                        | —                             | 5.13    |
| <b>Ketoprofen</b>       | 1.24E + 06                                       | 4.23E - 10                        | 1.27E - 06                    | 62.93   |
| <b>Clarithromycin</b>   | 1.93E + 06                                       | 1.65E - 06                        | 5.31E - 03                    | 34.20   |
| <b>Irbesartan</b>       | 1.22E + 06                                       | 4.51E - 08                        | 1.70E - 03                    | 75.95   |
| <b>Sulfamethoxazole</b> | 5.53E + 05                                       | 1.39E - 09                        | 6.59E - 03                    | 332.47  |

M3 [..<sup>141</sup> ]was preferred to the model M2, [..<sup>142</sup> ]despite less parsimonious in term of number of parameters (three instead of two). The comparison between observations and modeling results by the model M3 for the 5 selected compounds are shown in the Fig. 3 with the optimal set of parameters shown in Table 4.

Despite the lower number of parameters, concentrations of diclofenac along the Noce river are reproduced very well by a simplified version of the model M3 with two parameters. The likelihood function is two orders of magnitude smaller than for the other compounds ([..<sup>145</sup> ] $L = 5.13$ , see Table 4) and predicted concentrations are almost indistinguishable [..<sup>146</sup> ]from the observed ones (Fig. 3). The parameters of M3 in this case are 2, instead of 3, because no diclofenac was detected in summer and therefore only the winter  $k$  value was inferred from the data. The other compounds are well reproduced by the model M3 in both seasons, except irbesartan in summer at the sampling locations WB3B, WB4B and WB5B [..<sup>147</sup> ]and to some extent also ketoprofen in winter, particularly at the sampling locations WB4B and WB5B. The pharmaceutical with the highest L-value (i.e. the worst match with observations) is sulfamethoxazole with [..<sup>148</sup> ] $L = 332.47$  (Table 4). Overall, the [..<sup>149</sup> ]model M3 was able to capture the observed concentrations of PPCPs along the Noce river in both winter and summer campaigns. As expected (see Table 4), the inferred values of the decay rate  $k$  are lower in winter than in summer for all the compounds: this is due to the temperature dependence of biological processes causing degradation.

Figure 4 shows the likelihood function  $L$  given by Eq. (19) as a function of the model parameters for the model M3. In particular,  $L$  is represented in a two dimensional space as a function of  $\gamma$  and  $k$ , the latter being different in the two sampling campaigns (see the two columns of Fig. 4). [..<sup>150</sup> ]Notice that the model [..<sup>151</sup> ]allows a clear identifiability of the parameters for all the compounds, as shown by the relatively small dark blue areas corresponding to [..<sup>152</sup> ]low  $L$  values, located at large

<sup>141</sup>removed: , although it is less parsimonious than  
<sup>142</sup>removed: which however does not include this important process  
<sup>145</sup>removed:  $L = 3.11$ ,  
<sup>146</sup>removed: form  
<sup>147</sup>removed: , clarithromycin in winter  
<sup>148</sup>removed:  $L = 283.70$   
<sup>149</sup>removed: models succeed in representing the observed changes of PPCPs concentrations  
<sup>150</sup>removed: It is worth noting  
<sup>151</sup>removed: allowed  
<sup>152</sup>removed: small values of



**Figure 3.** Concentrations of 5 selected pharmaceuticals for both winter and summer campaigns. Red [..<sup>143</sup>]crosses represent modeling results obtained with the model M3, whereas blue [..<sup>144</sup>]plusses represent measured concentrations at the 5 selected locations along the Noce river. Diclofenac was detected only during the winter campaign.

distance from the boundaries of the parameters space. As expected, the optimal  $k$  values are smaller in winter than in summer, according to water temperature being lower in winter than in summer.

All the computations for the inference of the model parameters and the following application of the model illustrated in Sect. 5 have been performed by means of the programming software MATLAB (MATLAB, 2017).

## 5 Application at catchment scale

As an illustrative example, we applied our modeling framework to the whole Adige river with the objective of evaluating seasonal variations of PPCPs concentrations at a few relevant locations. The simulations were limited to the year 2015 for illustration purposes, but they can be extended over longer periods, including future projections, provided that hydrological and population data, both recorded or modeled, are available. The model, in particular, allows considering the interplay between hydrological and population variability, the latter due to touristic fluxes<sup>[.153]</sup>. Simulations were performed by using the model M3<sup>[.154]</sup> with the optimal parameters shown in Table 4<sup>[.155]</sup> and the S. Giustina and Mollaro reservoirs modeled as described in Sect. 4. The other reservoirs of the Adige catchment are either not intercepting release points or have a small volume and therefore were not included. Only WWTPs with maximum served population above 10,000 persons-equivalent were selected as release points for the simulations, and communities served with systems of smaller size were aggregated to the closest selected release point. Altogether 26 WWTPs release points were included into the model, obtaining a good spatial coverage (see Fig. 2). The monthly average number of persons actually served was obtained by aggregating the municipalities and the census data (including the touristic presences) to each release point .

It should be acknowledged that model's parameters are affected by uncertainty, which is expected to be large due to the limited number of data available for inference. For this reason the results of the simulations discussed here should be considered as a preliminary exploration providing uncertain estimates of concentrations at the sampling points. However, the simulated spatial pattern of the concentrations and its relative values are much more reliable than the absolute concentration at a given point, such that areas where the impact of PPCPs is stronger are reliably identified. This limitation is due to the lack of proper data and cannot be, by any means, attributed to limitations in the structure of the model.

The decay rates ( $k$ ), evaluated at the monthly scale, were obtained by means of the Arrhenius kinetics parameters ( $A$  and  $E_A$ ), considered constant for each one of the 5 pharmaceuticals and<sup>[.156]</sup> calculated from Eq. (18), given the two  $k$  values obtained by inversion of the observational data (see Table 5). For diclofenac the summer value of  $k$  was inherited by ketoprofen, which belongs to the same pharmacological class. Notice that  $k$  varies by orders of<sup>[.157]</sup> magnitude (i.e. in the range<sup>[.158]</sup>  $10^{-10} - 10^{-3} \text{ [s}^{-1}\text{]}$ ), between winter and summer, due to the seasonal fluctuations of water temperature. In winter the decay

<sup>153</sup>removed: evaluated at the daily scale

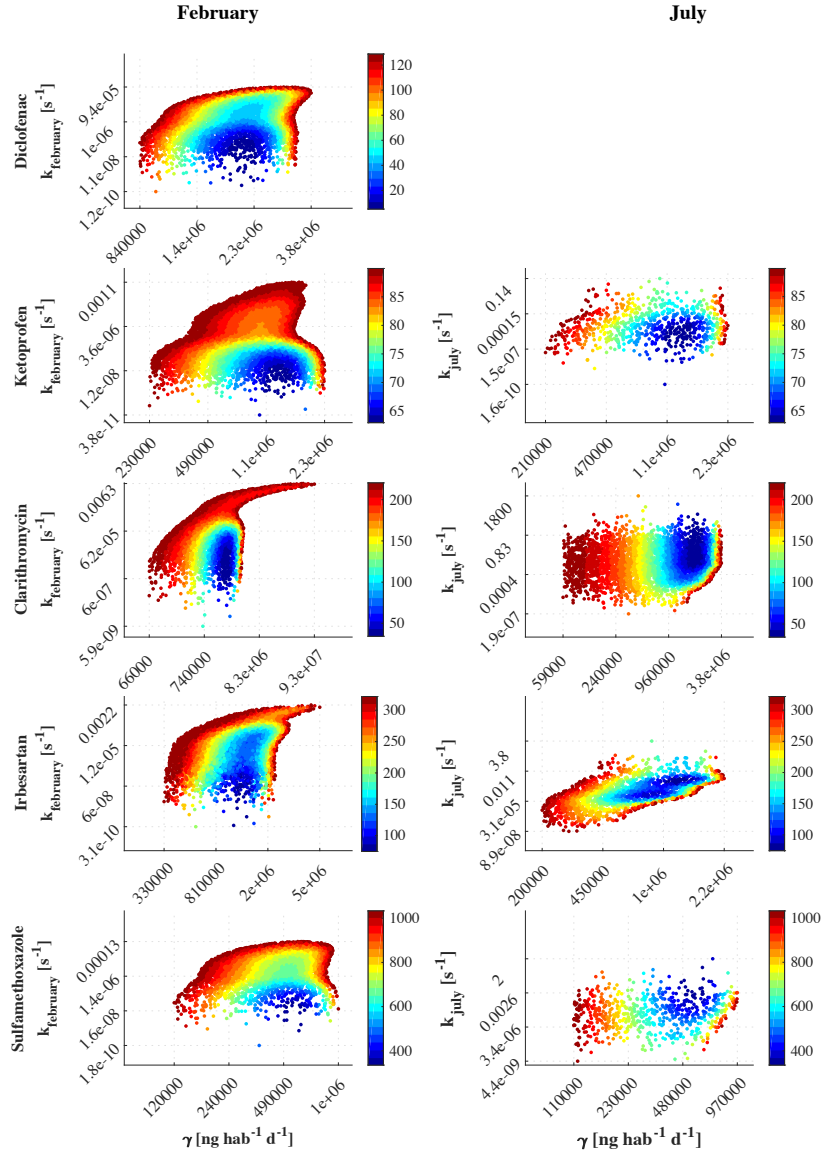
<sup>154</sup>removed: (see Sect. 4)

<sup>155</sup>removed: .

<sup>156</sup>removed: obtained from the inversion of

<sup>157</sup>removed: magnitudes

<sup>158</sup>removed:  $10^{-9} - 10^{-2}$



**Figure 4.** Objective function  $L$ , given by Eq. (19), as a function of the model's parameters for the 5 selected compounds. The left and right columns refer to winter and summer campaign, respectively. Each dot at the position sampled by the latin hypercube technique assumes the color corresponding to the scale for  $L$  shown on the right of each panel. For clarity, pairs of  $k$  and  $\gamma$  resulting in values of  $L$  larger than the 0.1 quantile are not shown.

rate is rather small for all compounds, suggesting dilution as the main attenuation mechanism which, on the other hand, in winter is at its minimum due to low streamflow. In summer the decay rate is significantly higher, resulting in a concurrent effect of biological decay and dilution, which is higher than in winter due to snowmelting, for all the compounds. In terms of half-life time, July is the month with the fastest decays (half life of [..<sup>159</sup>]95 h for diclofenac and ketoprofen, [..<sup>160</sup>]2.6 min for clarithromycin, [..<sup>161</sup>]7 min for irbesartan and [..<sup>162</sup>]22 s for sulfamethoxazole), whereas December and January are the months with the slowest decays (half life of [..<sup>163</sup>]43 y for diclofenac, [..<sup>164</sup>]15.4 y for ketoprofen, [..<sup>165</sup>]6.4 d for clarithromycin, [..<sup>166</sup>]3.8 y for irbesartan and [..<sup>167</sup>]4.5 y for sulfamethoxazole). Notice that in winter none of the 5 compounds analyzed in the present [..<sup>168</sup>]study can be considered as biologically decaying, since their half life is significantly larger than the residence time.

10 [..<sup>171</sup>]

Figure 5 shows the [..<sup>172</sup>]annual average of the simulated concentrations for the 5 compounds (panels from (a) to (e)[..<sup>173</sup>]) along the Adige main stem and its tributaries. The highest mean concentrations were obtained for diclofenac (panel a), particularly in the [..<sup>174</sup>]middle course of the main stem and in the Eastern portions of the basin. The relatively high concentrations in the upper [..<sup>175</sup>]Rienza and Avisio rivers (see Fig. 2 for the location of the Adige's tributaries) [..<sup>176</sup>]is a consequence of the combined effect of low dilution and high PPCPs load due to the touristic presences[..<sup>177</sup>]. Intermediate values [..<sup>178</sup>]are observed in the Noce [..<sup>179</sup>]middle stem and in the [..<sup>180</sup>]southernmost portion of the Adige river. Also ketoprofen (panel b) [..<sup>181</sup>]shows concentrations higher than [..<sup>182</sup>]100 ng/l, [..<sup>183</sup>]in particular downstream of the WWTP

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<sup>159</sup>removed: 6

<sup>160</sup>removed: 2.1

<sup>161</sup>removed: 6.5

<sup>162</sup>removed: 21

<sup>163</sup>removed: 19.3

<sup>164</sup>removed: 5.5

<sup>165</sup>removed: 15

<sup>166</sup>removed: 22

<sup>167</sup>removed: 2.3

<sup>168</sup>removed: work

<sup>171</sup>removed: Only WWTPs with maximum served population higher than 10,000 persons-equivalent were selected as release points for the simulations, and communities served with systems of smaller size were aggregated to the closest selected release point. Altogether 26 WWTP release points were included into the model, obtaining a good spatial coverage (see Fig. 2). The number of persons actually served was computed at the monthly time scale based on the municipalities aggregated to each release point and the census data (including the touristic presences).

<sup>172</sup>removed: average annual concentrations of the

<sup>173</sup>removed: in the figure

<sup>174</sup>removed: Southern and

<sup>175</sup>removed: parts of the

<sup>176</sup>removed: may be justified by

<sup>177</sup>removed: , whereas the high concentrations in the lower part of the Adige main stem are due to the relatively high input loads of the city of Trento

<sup>178</sup>removed: were

<sup>179</sup>removed: upper

<sup>180</sup>removed: Adige river just upstream the city of Trento

<sup>181</sup>removed: and irbesartan (panel d) show

<sup>182</sup>removed: 10<sup>3</sup>

<sup>183</sup>removed: both in the

**Table 5.** Monthly decay rates ( $k$  [s<sup>-1</sup>]) of the 5 selected compounds, computed by using the Arrhenius law (Eq. [..<sup>169</sup> ]18) [..<sup>170</sup> ] with the values of  $A$  [s<sup>-1</sup>] and  $E_A$  [kJmol<sup>-1</sup>], obtained by inverting Eq. (18) with reference to the decay rate inferred from the observational data of February and July 2015 (first two rows).

|                                    | Diclofenac     | Ketoprofen     | Clarithromycin | Irbesartan     | Sulfamethoxazole |
|------------------------------------|----------------|----------------|----------------|----------------|------------------|
| $A$ [s <sup>-1</sup> ]             | $9.32E + 72$   | $2.17E + 73$   | $2.46E + 79$   | $5.60E + 117$  | $1.15E + 152$    |
| $E_A$ [kJmol <sup>-1</sup> ]       | $4.36E + 02$   | $4.36E + 02$   | $4.51E + 02$   | $6.65E + 02$   | $8.51E + 02$     |
| $k$ (January) [s <sup>-1</sup> ]   | $2.20E - 10$   | $5.16E - 10$   | $1.28E - 06$   | $7.90E - 09$   | $8.05E - 10$     |
| $k$ (February) [s <sup>-1</sup> ]  | $2.70E - 10^*$ | $6.34E - 10^*$ | $1.58E - 06^*$ | $1.08E - 08^*$ | $1.20E - 09^*$   |
| $k$ (March) [s <sup>-1</sup> ]     | $3.33E - 09$   | $7.82E - 09$   | $2.11E - 05$   | $4.96E - 07$   | $1.61E - 07$     |
| $k$ (April) [s <sup>-1</sup> ]     | $1.18E - 08$   | $2.77E - 08$   | $7.79E - 05$   | $3.40E - 06$   | $1.90E - 06$     |
| $k$ (May) [s <sup>-1</sup> ]       | $4.38E - 08$   | $1.03E - 07$   | $3.02E - 04$   | $2.51E - 05$   | $2.45E - 05$     |
| $k$ (June) [s <sup>-1</sup> ]      | $8.94E - 08$   | $2.10E - 07$   | $6.31E - 04$   | $7.45E - 05$   | $9.88E - 05$     |
| $k$ (July) [s <sup>-1</sup> ]      | $7.37E - 07$   | $1.73E - 06^*$ | $5.56E - 03^*$ | $1.85E - 03^*$ | $6.04E - 03^*$   |
| $k$ (August) [s <sup>-1</sup> ]    | $1.82E - 07$   | $4.26E - 07$   | $1.31E - 03$   | $2.19E - 04$   | $3.93E - 04$     |
| $k$ (September) [s <sup>-1</sup> ] | $3.37E - 08$   | $7.92E - 08$   | $2.31E - 04$   | $1.69E - 05$   | $1.48E - 05$     |
| $k$ (October) [s <sup>-1</sup> ]   | $6.94E - 09$   | $1.63E - 08$   | $4.51E - 05$   | $1.52E - 06$   | $6.75E - 07$     |
| $k$ (November) [s <sup>-1</sup> ]  | $3.81E - 09$   | $8.94E - 09$   | $2.43E - 05$   | $6.08E - 07$   | $2.09E - 07$     |
| $k$ (December) [s <sup>-1</sup> ]  | $2.20E - 10$   | $5.16E - 10$   | $1.28E - 06$   | $7.90E - 09$   | $8.05E - 10$     |

\* inferred  $k$  values.

of Bolzano, labelled as 14 in Fig. 2 (see Table B1 in the Appendix B). For all the compounds, concentrations are relatively high in the headwaters of the Rienza river (i.e. upper Gadera catchment), where the touristic presences are high in winter[..<sup>184</sup> ]. In general, concentrations of all pharmaceuticals show a remarkable spatial variability with values ranging from 0 to [..<sup>185</sup> ]200 ng/l with maximum in the [..<sup>186</sup> ]central and North-Eastern portion of the basin. This entails that local pharmaceutical consumption affects remarkably the detected concentrations in rivers and, in some cases, overwhelms natural dilution [..<sup>187</sup> ]which varies linearly with water discharge. Notice that in the lower part of the Adige main stem, after the confluence with the Noce and Avisio tributaries, concentrations decrease for all the compounds. This is due to both the attenuating effect of dilution at the nodes and mixing within both S. Giustina and Mollaro reservoirs, in the middle course of the Noce.

During the two sampling campaigns samples were collected and concentrations evaluated at the sites WB6, just up-stream of the city of Trento and the confluence of both Noce and Avisio, and at four locations labelled WB7 A, B, C and D, downstream of Trento (see Mandaric et al. (2017) for locations). This additional information cannot be used for a formal validation because representative of the sampling day, while simulations are conducted at the monthly scale because

<sup>184</sup> removed: , and in the southernmost Adige main stem, downstream the confluence with the Leno river

<sup>185</sup> removed:  $2.5E + 3$

<sup>186</sup> removed: North-Eastern and in the Southern portions

<sup>187</sup> removed: that acts proportionally to the water discharge.

along the main stem of the Adige river census data are available only at this scale for the touristic fluxes and at the annual scale for the resident population. While one can safely assume that resident population changes little within a year, touristic fluxes show significant variations at the weekly and even shorter time scales. Monthly concentrations produced by the model at selected sections are discussed below keeping in mind this limitation.

- 5 Figure 6 shows the monthly average of flux concentrations at the following 4 selected control sections (see Fig. 2): Soraga in the upper Avisio river; Vermiglio in the Vermigliana creek (headwaters of the Noce river); Ponte Adige along the Adige river before the confluence with the Isarco river (draining the Northwestern portion of the Adige catchment) and Bolzano in the Isarco river at the confluence with the Adige river. These control sections were selected because official gauging stations with a significant drainage basin. [..<sup>188</sup> ]Diclofenac is present at all gauging stations [..<sup>189</sup> ]with concentrations up to 300 ng/l at
- 10 Soraga and Vermiglio in the upper Avisio and Noce, respectively (Vermiglio is located at the lower end of the Vermigliana creek, a tributary of the Noce). For comparison see also the annual mean [..<sup>190</sup> ]values shown in Fig. 5[..<sup>191</sup> ]. On the other hand, sulfamethoxazole shows the lowest concentrations, due to the [..<sup>192</sup> ]modest input loads (see Table 4)[..<sup>193</sup> ]. The temporal pattern of diclofenac and ketoprofen is characterized by two peaks, one between February and March and the other in August[..<sup>194</sup> ], following the seasonal pattern of touristic fluxes. The other pharmaceuticals are without the
- 15 summer peak, but show a slight increase in autumn before the winter peak. These patterns are shaped by the interplay between dilution and decay, which are both higher in summer than in winter due to snow melting and higher temperatures, respectively. The importance of streamflow seasonality is clearly evident in the low concentrations observed between April and June when [..<sup>195</sup> ]
- [..<sup>196</sup> ]snow melting, and therefore streamflow, are at their maximum. Decay, instead, is more effective in reducing the
- 20 summer concentrations of clarithromycin, irbesartan and sulfamethoxazole rather than that of the anti-inflammatories, according to their higher decay coefficients (see Table 4 and Table 5). At Vermiglio a second peak in August [..<sup>197</sup> ]is less pronounced with respect to the other control sections. [..<sup>198</sup> ]This attenuation is justified by lower touristic fluxes with respect to winter (i.e. [..<sup>199</sup> ]2,824 persons per day on average served by the WWTP at Passo del Tonale in August 2015 against [..<sup>200</sup> ]4,166 in February of the same year) and to the streamflow contribution from summer melting of Presanella and

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<sup>188</sup>removed: Diclofenac shows the highest concentrations

<sup>189</sup>removed: (

<sup>190</sup>removed: value

<sup>191</sup>removed: ) whereas sulfamethoxazole

<sup>192</sup>removed: lower

<sup>193</sup>removed: , shows the smallest concentrations. The other pharmaceuticals show temporal patterns similar to diclofenac with

<sup>194</sup>removed: . The dilution effect of snow melting

<sup>195</sup>removed: snow-melting is at its maximum.

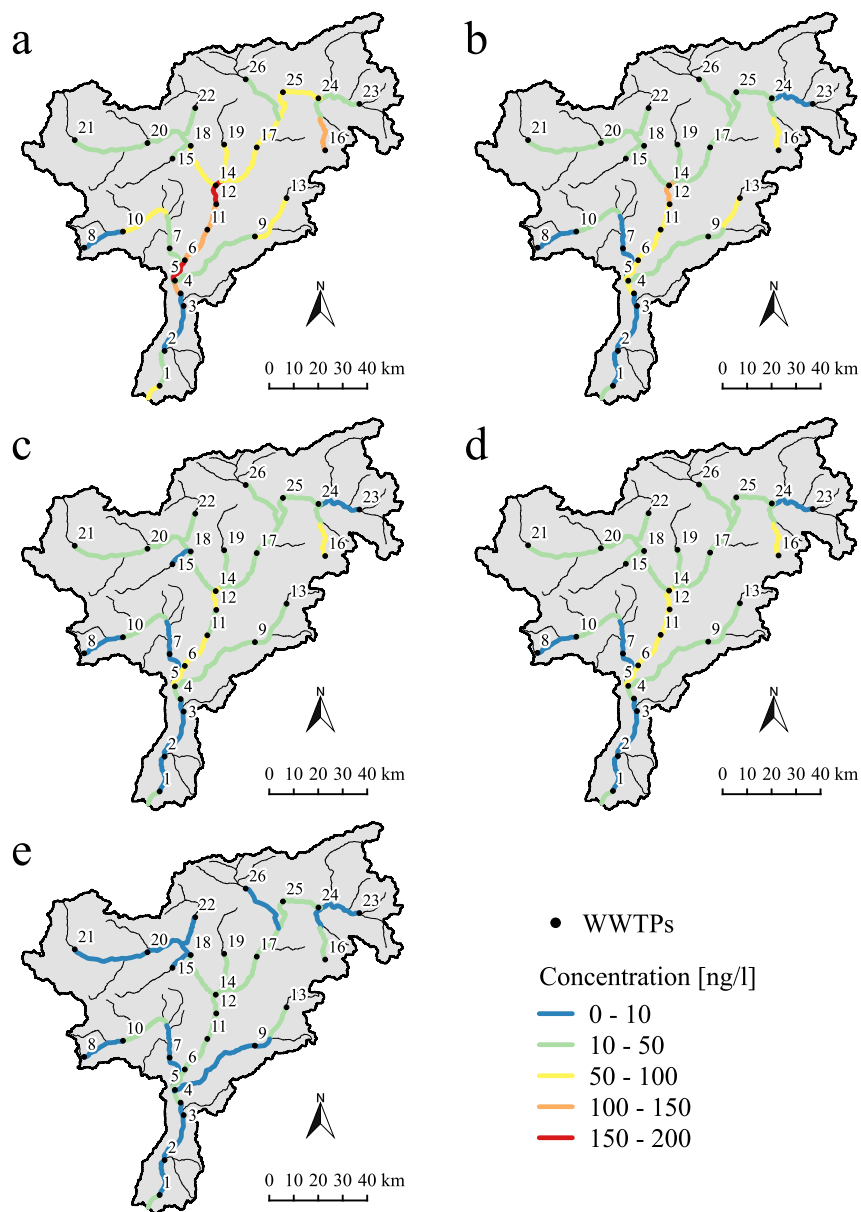
<sup>196</sup>removed: Vermiglio differs from the other three selected control sections: it shows a remarkable concentration peak in February, followed by a rapid attenuation in the melting season and a much less pronounced

<sup>197</sup>removed: ,

<sup>198</sup>removed: The attenuation of the second peak

<sup>199</sup>removed: 30,000 persons

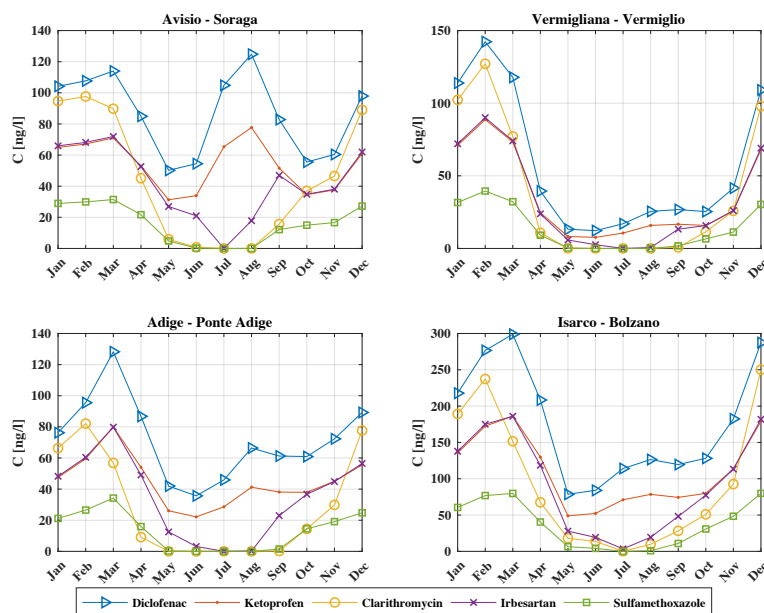
<sup>200</sup>removed: 70,000



**Figure 5.** Annual mean concentrations of (a) diclofenac, (b) ketoprofen (c) clarithromycin (d) irbesartan (e) sulfamethoxazole in the Adige catchment for the year 2015. The position of WWTPs along the river network are marked with a black bullet and numbered progressively from the Southern control section in the main stem of the Adige river to the headwaters (see Table B1 in the Appendix B). The lowest concentrations are marked in blue, whereas the higher concentrations in red.

Presena glaciers which maintains high streamflow also after the end of [<sup>201</sup>]the snowmelting season (see e.g., Chiogna

<sup>201</sup>removed: snowmelting season (see e.g., Chiogna et al., 2016). The simulated concentrations are higher in winter than in summer also at the control section of Bolzano. The summer peak is remarkable for diclofenac and ketoprofen, but much less pronounced for the other compounds. Conversely, the



**Figure 6.** Monthly flux concentration of 5 PPCPs (diclofenac, ketoprofen, clarithromycin, irbesartan and sulfamethoxazole) at the control sections of Soraga in the Avisio river, Vermiglio in the Vermigliana creek, Ponte Adige in the Adige river and Bolzano in the Isarco river. Concentrations are expressed in  $ng/l$ .

et al., 2016, and Table 2). The highest peak at Soraga is observed in August, and this is in agreement with the higher touristic presences in summer with respect to winter (about [..<sup>202</sup>] 25,000 and 19,000 persons per day served by the upstream WWTP of Pozza di Fassa in August and February 2015, respectively), while the contribution from the Marmolada glacier is diverted outside the basin through the Fedaia reservoir (see e.g., PAT, 2012), thereby [..<sup>203</sup>] reducing dilution. Conversely, at Ponte Adige the [..<sup>204</sup>] winter peak is higher than in [..<sup>205</sup>] summer, showing a complex interplay between variability of streamflow and touristic presences. Also at Bolzano the simulated concentrations are higher in winter than in summer. In addition, here the modeled concentrations are [..<sup>206</sup>] higher than in the other control sections ([..<sup>207</sup>] see also Fig. 5).

These simulations showed that concentrations of PPCPs changed through the seasons [..<sup>208</sup>] depending on both population dynamics and hydrological characteristics of the year [..<sup>209</sup>]. This behavior cannot be identified when a single emission and representative water discharge are adopted, as commonly done in applications.

<sup>202</sup>removed: 463 and 262 thousand persons

<sup>203</sup>removed: attenuating dilution. Also

<sup>204</sup>removed: summer peak was

<sup>205</sup>removed: winter

<sup>206</sup>removed: lower

<sup>207</sup>removed: notice the different scales in the Fig. 6 and

<sup>208</sup>removed: with a behavior that depends on

<sup>209</sup>removed: : a behavior that

## 6 Discussion and Conclusions

In the present paper we proposed a simplified, yet realistic, transport model of pharmaceuticals and personal care products in a river network. The model takes into account [..<sup>210</sup>]time variability of both hydrological fluxes and emissions from the waste water treatment plants and other sources at daily or larger scales, thereby overcoming the main limitations of the existing approaches, which assume both processes as [..<sup>211</sup>]time invariant. Emissions are computed by considering available data on consumption of pharmaceuticals and personal care products and population living within the catchment, including touristic fluxes, which are becoming more and more important since touristic activities expanded tremendously in the [..<sup>212</sup>]past decades. Attenuation processes are dilution and bio-geochemical decay, the former included by considering streamflow variable at the [..<sup>213</sup>]proper scale and the latter by a first-order irreversible decay reaction. The effect of lakes, or reservoirs, is included in our modeling approach by adding the pdfs of the residence time, which shape depends on the mixing characteristics of the reservoirs, to the convolution chain.

The model was applied to the Adige river basin, North-East of Italy, by considering a selection of five pharmaceuticals, which presence was detected in two sampling campaigns conducted in February and July 2015, belonging to the groups of analgesic/anti-inflammatory, antibiotic and antihypertensive. Four different parametrizations of the model, corresponding to different hypotheses on the variability of the per-capita emission rate (i.e.  $\gamma$ ) and the decay rate (i.e.  $k$ ), have been considered and the corresponding parameters were obtained by inversion of the observational data collected in the two sampling campaigns. The best performing parametrization was identified, according to the Akaike information criterion. The selected parametrization of the model includes a constant in time  $\gamma$ , such that variability of the emissions follows changes in the population, which is high in the Alpine area due to important touristic fluxes in winter and summer seasons, and a decay rate  $k$  varying as a function of water temperature through the Arrhenius law. This three-parameter model has been applied at monthly time scale to the whole Adige catchment [..<sup>214</sup>]for the year 2015. The inferred monthly concentrations at 5 sections not used for calibration are in line with those measured during the sampling campaigns, revealing the capability of the model to reproduce spatial and temporal patterns of concentration.

Monthly flux concentrations at four relevant gauging stations showed a significant seasonal variability as it was expected considering the large fluctuations of touristic presences and the strong seasonality of streamflow. In general, decay processes, as epitomized by the decay rate  $k$ , are less important than dilution due to both streamflow variability and the contribution from sub-catchments slightly or not impacted by pharmaceutical releases. In winter, when dilution is low, the decay rate is also at its minimum because of the low water temperature[..<sup>215</sup>]. On the other hand, in summer the relevance of a high decay rate due to the high temperature is diminished by the overwhelming effect of dilution. Among the five selected pharmaceuticals,

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<sup>210</sup>removed: transient conditions

<sup>211</sup>removed: stationary

<sup>212</sup>removed: last

<sup>213</sup>removed: monthly

<sup>214</sup>removed: and

<sup>215</sup>removed: , while in summer despite the decay rate is high its relevance

diclofenac and ketoprofen are those less affected by decay, while <sup>216</sup>clarithromycin and sulfamethoxazole are the compounds subject to the highest decay. Overall, the proposed modeling approach shows seasonal and spatial patterns of solute concentrations in the stream water, which cannot be detected with existing approaches inherently <sup>217</sup>time invariant. Touristic fluxes and streamflow variability are the driving factors of these patterns, and should be carefully considered and estimated in applications. Indeed, the effects of streamflow and touristic fluctuations in the concentration patterns are intertwined, to an extent that depends on the particular compound and local conditions, and worth to be further analyzed to obtain reliable estimate of the impact on the freshwater ecosystem. Finally, our modeling framework is structured in a way that allows its use in combination with hydro-climatological models to elaborate <sup>218</sup>future scenarios.

*Code and data availability.* The MATLAB code of the model and the data obtained from the sampling campaigns are available upon request. All the other data needed for the reproducibility of the results are freely available and the sources are reported in Sect. 3.2.

## Appendix A: Scaling coefficients of the stream velocity

Dodov and Fofoula-Georgiou (2004) proposed the following scaling laws for the coefficients  $\Phi$  and  $\Psi$  of the geometry hydraulic expression <sup>219</sup>(Eq. 3):

$$\Phi(A) = \exp[-(\alpha_{C_A} + \beta_{C_A} \ln(A)) + (\alpha_Q + \beta_Q \ln(A)) \Psi_{C_A}] \quad (A1)$$

with

$$\Psi_{C_A}(A) = \left[ \frac{\gamma_{C_A} + \delta_{C_A} \ln(A)}{\gamma_Q + \delta_Q \ln(A)} \right]^{1/2} \quad (A2)$$

and finally the exponent  $\Psi$  is given by:

$$\Psi(A) = 1 - \Psi_{C_A}(A) \quad (A3)$$

In all these expressions  $A$  [km<sup>2</sup>] is the contributing area and the other coefficients are reproduced in the Table A1 (see also Table 3 of the paper by Dodov and Fofoula-Georgiou (2004)).

<sup>216</sup>removed: sulfamethoxazole is the compound

<sup>217</sup>removed: stationary

<sup>218</sup>removed: credible

<sup>219</sup>removed: of Eq. (

**Table A1.** Parameters of the scaling coefficients by Dodov and Foufoula-Georgiou (2004).

| Hydraulic geometry<br>factors | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ |
|-------------------------------|----------|---------|----------|----------|
| $C_A$                         | -3.1802  | 0.6124  | 0.8404   | 0.1130   |
| $Q$                           | -5.5428  | 0.7992  | 2.6134   | 0.0012   |

**Appendix B:** [..<sup>220</sup>] Location of the Waste Water Treatment Plants of the Adige river

The Table B1 shows the identification number used in the map of Fig. 2 to locate the WWTPs with maximum capacity larger than 10,000 person-equivalent installed in the Adige catchment.

<sup>220</sup>removed: WWTPs coordinates

**Table B1.** List of the WWTPs with maximum capacity of more than 10,000 person-equivalent considered in the application at catchment scale. The assigned identification numbers (ID) are sorted by latitude (from the southernmost to the northernmost plant) and the coordinates are expressed in [m] (UTM WGS 84).

| <i>ID</i> | <i>Name</i>        | <i>Easting [m]</i> | <i>Northing [m]</i> |
|-----------|--------------------|--------------------|---------------------|
| 1         | Ala                | 654586             | 5067957             |
| 2         | Rovereto           | 656654             | 5082229             |
| 3         | Trento Sud         | 664445             | 5100590             |
| 4         | Trento Nord        | 663193             | 5105707             |
| 5         | Lavis              | 660857             | 5110902             |
| 6         | Mezzocorona        | 664890             | 5119257             |
| 7         | Campodenno         | 658702             | 5124097             |
| 8         | Passo Tonale       | 623766             | 5124390             |
| 9         | Tesero             | 693548             | 5128973             |
| 10        | Mezzana            | 639633             | 5130966             |
| 11        | Termeno            | 674101             | 5131753             |
| 12        | Bronzolo           | 677758             | 5142131             |
| 13        | Pozza di Fassa     | 706482             | 5144652             |
| 14        | Bolzano            | 677544             | 5149815             |
| 15        | San Pancrazio      | 659866             | 5160771             |
| 16        | Sompunt            | 722274             | 5164161             |
| 17        | Bassa Valle Isarco | 694302             | 5165355             |
| 18        | Merano             | 667329             | 5166009             |
| 19        | Sarentino          | 680981             | 5166517             |
| 20        | Media Val Venosta  | 649646             | 5167136             |
| 21        | Alta Val Venosta   | 619907             | 5168345             |
| 22        | Passiria           | 669174             | 5181457             |
| 23        | Wasserfeld         | 736247             | 5183152             |
| 24        | Tobl               | 719504             | 5185433             |
| 25        | Bassa Pusteria     | 704999             | 5187904             |
| 26        | Wipptal            | 689775             | 5193172             |

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