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# 1 **SWATLitho: a hydrogeochemical model to estimate daily geochemical loads at the** 2 **catchment scale.**

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12

## 13 **Highlights**

- 14 • A lithological layer coupled to SWAT Hydrological Response Units has been introduced.
- 15 • A simple model has been implemented to assess daily cation and anion fluxes.
- 16 • Daily geochemical loads have been estimated using SWAT water balance.

## 17 **Abstract**

18 The increase in water salinisation in catchments has led to increased concern in assessing major ion loadings  
19 in freshwater environments. In this study, we couple a globally fitted model on chemical weathering to the  
20 Soil and Water Assessment Tool (SWAT) for the estimation of daily geochemical loadings at the catchment  
21 scale, "SWATLitho". The enhancements include *i*) a modification on the discretisation of the catchment area  
22 by integrating a layer describing lithology (QSWATLitho), and *ii*) the development of an extra module to  
23 compute the ionic loads derived from the chemical weathering of rocks. The model is sensitive to input data  
24 resolution, yielding the best results when including local data. Larger spatial and temporal discrepancies are  
25 found in one tributary, associated with point sources impacting the loadings; while these discrepancies are  
26 lower at headwater subbasins. Results suggest that, despite of these discrepancies, the average simulation of  
27 the daily ionic loadings is reasonable.

## 28 **Keywords**

29 Model coupling; Geochemical loadings; Chemical weathering; Downscaling

## 30 **1 Introduction**

31 Chemical quality assessment of river waters is crucial for understanding and assessing the potential impacts of  
32 threats to biodiversity, drinking water safety, and crop yields (Cañedo-Argüelles et al., 2018, Kaushal et al.,  
33 2017). One of these threats is the rise in major ion concentration, i.e. salinisation (Meybeck and Helmer,  
34 1989), which, despite having a relevant role in efficient ecosystem management (Cañedo-Argüelles et al.,  
35 2018), has received little attention in the past. Traditionally, two approaches tackling freshwater chemical  
36 assessments exist: the analysis of water samples framed within a monitoring program (e.g. Martínez-Santos et  
37 al., 2015), and the use of hydrogeochemical models to simulate the study area and possible scenarios (e.g.  
38 M’Nassri et al., 2019). Water sampling is a common practice in many places, yielding real valuable data, but  
39 spatially and temporally homogeneous information is obtained through modelling. The integration of these  
40 two approaches complements the assessment of chemical threats.

41 Models may be based on physical laws or data-regression equations for representing the system object of the  
42 study, being classified as mechanistic or empirical, respectively. Nowadays, there exists a number of  
43 mechanistic hydrogeochemical models, such as PHREEQC (Version 3 in Parkhurst and Appelo, 2013),  
44 MINTEQA2 (Allison et al., 1991), or WITCH (Goddéris et al., 2006), but their applicability is commonly  
45 limited to areas where extensive necessary data (mineral abundance, the chemical profile of soil water, initial  
46 boundary condition, etc.) is available as input. In other cases, simplifications or assumptions are needed in  
47 order to apply this kind of model, increasing the model’s prediction uncertainty. A different solution is to  
48 develop simpler models to replace these complex configurations (Schoups et al., 2006).

49 As an alternative to mechanistic models, several empirical models focusing on single-processes have been  
50 built, such as the Global Erosion Model for CO<sub>2</sub> (GEM-CO<sub>2</sub>, Amiotte-Suchet and Probst, 1995), the Chemical  
51 Weathering Rate model (CWR, Hartmann et al., 2014) and Ionic fluxes derived from Chemical Weathering of  
52 Rocks model (ICWR, Lechuga-Crespo et al., 2020a), which have yielded a static output over worldwide scale  
53 assessments, i.e. the annual average result, regarding chemical weathering rates and associated products  
54 (atmospheric CO<sub>2</sub> consumption, P-release, ionic loadings to rivers, etc.). To date and to the best of the  
55 authors’ knowledge, none of them have been tested on a local scale and under a dynamic approach, while  
56 management decisions are usually taken at a catchment scale and need the temporal evolution within a year.

57 In the present study, an empirically-based model has been coupled to a physically-based hydrological model  
58 to compute daily geochemical loadings from the chemical weathering of rocks. The SWAT model has long  
59 been used to quantify the loads and concentrations of matter and nutrients from land to the catchment’s outlet  
60 (Arnold et al., 2012, Fu et al., 2019), as well as its evolution at different time scales. However, it is not  
61 possible to estimate the geochemical loadings with this model, as there is no subroutine or module  
62 implemented with this purpose. In this sense, the ICWR model (Lechuga-Crespo et al., 2020a) has been  
63 applied to the global scale. It has yielded the first map on average annual ionic fluxes, derived from the

64 chemical weathering of rocks to rivers. Nevertheless, its ability to simulate the dynamics of chemical  
65 weathering derived ionic loads and its performance on local catchments have not been tested yet.

66 In this sense, the coupling of the SWAT and ICWR models poses an opportunity to evaluate spatially-explicit  
67 geochemical fluxes, since a basin's hydrology in SWAT is described using the Hydrological Response Unit's  
68 (HRU) semi-distributed approach . Consequently, ionic loadings from chemical weathering may be assessed  
69 and, if the atmospheric contribution is known, this tool may work with observed data to estimate how much  
70 anthropogenic saline effluent found in a catchment. It is important to note that a similar approach has been  
71 recently published by Bailey et al. (2019), where they present the coupling of a mechanistic model for major  
72 ion chemical partitioning within the SWAT hydrological code. Such mechanistic methodology presents the  
73 same constraints in application as the other mechanistic approaches: the availability of input data and the  
74 establishment of boundary conditions for simulation.

75 The objective of this study is to downscale the ICWR model spatially and temporally as well as explore the  
76 performance in a case study where a geochemistry monitoring program has been taken. This case is  
77 exploratory, and the model objectives are to simulate the daily geochemical loads of major ions and their  
78 spatial distribution. Given the modelling framework and the constraints of both models, the processes to be  
79 simulated are chemical weathering of rocks, mass transport, and routing from catchment subbasins to the  
80 outlet. The model's spatial definition is conditioned by the HRU delimitation of the modified model (which is  
81 explained in Section 2.2), while the simulation's time-step is daily. A chemical equilibrium is assumed  
82 between rock and water at the temporal scale of simulation. Then, loadings are expected to be dependent on  
83 the discharge distribution among groundwater, lateral, and surface fluxes; the lithological groups in the  
84 underlying rock; and the soil types.

## 85 **2 Methods**

### 86 **2.1 Overview of the SWAT and the ICWR models**

87 The Ionic fluxes derived from Chemical Weathering of Rocks (ICWR, [Lechuga-Crespo et al., 2020a](#)) model is  
88 empirically based and its parameters have been fitted at a global scale for the estimation of spatially explicit  
89 fluxes of chemical weathering of rocks  $F$ , measured in  $\text{mol}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$  for each major ion  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  
90  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and alkalinity (commonly associated with  $\text{HCO}_3^-$ ). The model configuration is based on the  
91 multivariable regression shown in Equation 1. The input data needed for this model includes the specific  
92 discharge  $q_{ann}$  measured in mm, the lithological composition of the rocks  $L_i$  expressed as the percentage of the  
93 catchment area covered by a lithological group, the soil covering the bedrock layer for the estimation of the  
94 soil shielding effect factor  $f_{sx}$ , which is different for each ion  $x$ , and the parameter of the equation  $C_{xi}$ ,  
95 representing the water concentration on every ion. Further explanation of the development, calibration, and  
96 limitations of the model can be seen in [Lechuga-Crespo et al. \(2020a\)](#). The output of this model is an annual  
97 average specific flux of major ion loads originating from the chemical weathering of rocks to rivers, which,

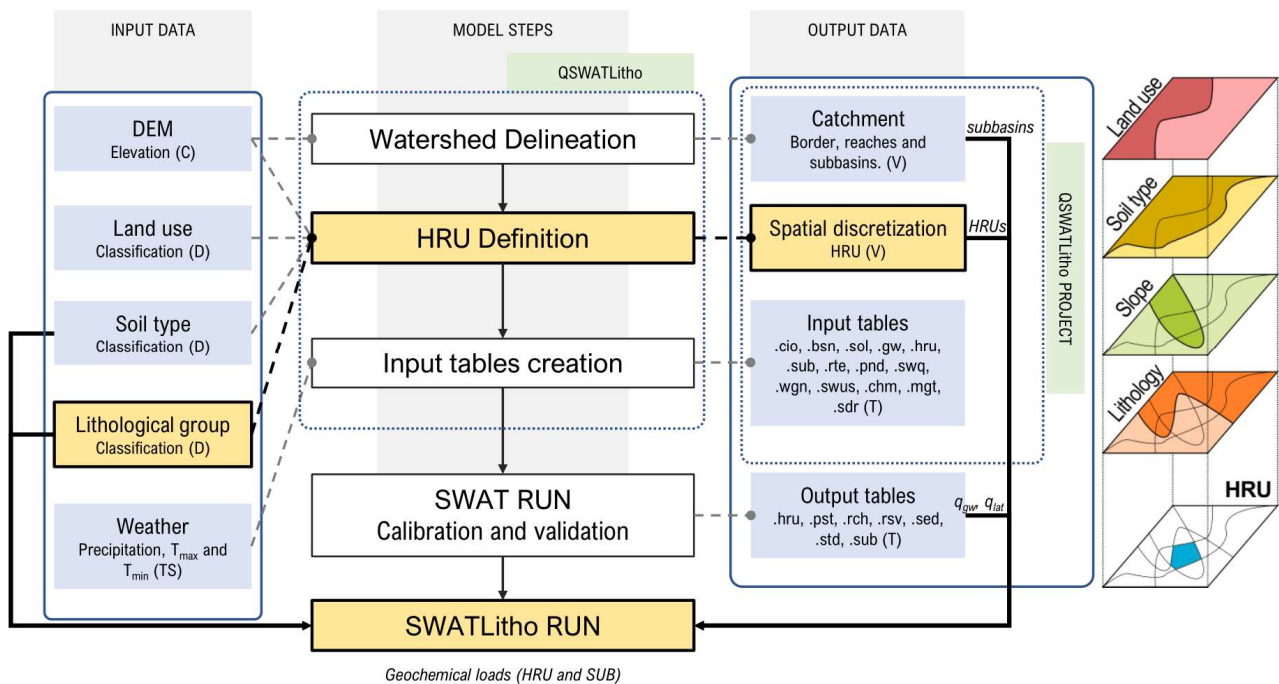
98 together with atmospheric deposition and anthropogenic inputs, is the main reservoir of saline exports of a  
 99 basin.

100 
$$F_x = q_{ann} \cdot f_{s_x} \cdot \sum L_i \cdot C_{x_i} \quad \text{Equation 1}$$

101 The SWAT is a physically based and semi-distributed model developed to assess water, sediments, and  
 102 nutrients in agronomic catchments at yearly, monthly, daily, and sub-daily time steps (Arnold et al., 1998).  
 103 Water, matter, and nutrient balances are simulated in homogeneous spatial units, HRUs, a combination of  
 104 unique slope, land use, and soil type areas, which are then aggregated to the subbasin scale and routed through  
 105 tributaries and channels towards the outlet of the catchment. The HRUs, together with the weather data (at  
 106 least precipitation and temperature time series), provide the input data for the simulation. A more detailed  
 107 description of the model is available in the SWAT2012 theoretical handbook (Neitsch et al., 2011).

108 **2.2 Coupling the ICWR model to SWAT**

109 The approach to spatially discretising the catchment area in the SWAT model has been modified to include a  
 110 fourth layer in the definition of the HRUs: the lithological groups. This modification has been performed in  
 111 the QGIS geographic information system plugin used to set up the model, QSWAT (Dile et al., 2016); the  
 112 modified version is hereby called QSWATLitho. The SWAT code has not been modified to maintain the  
 113 possibility of using external software, such as SWAT CUP (Abbaspour et al., 2007), for autocalibration.  
 114 Instead, an extra module (SWATLitho.py) has been written to read the QSWATLitho and SWAT outputs and  
 115 compute the geochemical fluxes and loads. The workflow of the model's configuration is shown in Figure 1.



116 **Figure 1.** Workflow summary of the ICWR model implemented on the modified QSWAT. The modifications  
 117 accomplished in the input data, model steps, and output data are highlighted in yellow (the reader is referred to  
 118

119 the online version for the colour appreciation). Bold arrows indicate the input data for the SWATLitho module  
120 for the estimation of the geochemical loads. On the right side, there is a conceptual representation of the new  
121 delimitation of the HRUs.

### 122 2.2.1 QSWATLitho

123 Traditionally, a QSWAT model setup consists of three main phases: the delineation of the watershed and  
124 subbasins, the delimitation of the HRUs, and the write of the input tables for SWAT modelling. For the  
125 QSWATLitho implementation, the second step has been modified by changing the *hrus.py*, *DBUtils.py*, and  
126 *QSWATUtils.py* files in the original plugin, causing the inclusion of a new layer to the delimitation of the  
127 HRUs. Now, every HRU contains a unique combination of slope, land use, soil type, and lithological group,  
128 and the water balance is defined for each one of them. The first consequence of this change is an increased  
129 number of HRUs when setting up a project, causing a finer definition on the spatial distribution of the model  
130 outputs and an increase in the time used for the SWAT simulation. The QSWATLitho may be found and  
131 downloaded at <https://swat.tamu.edu/software/swat-litho/>.

### 132 2.2.2 ICWR module - SWATLitho

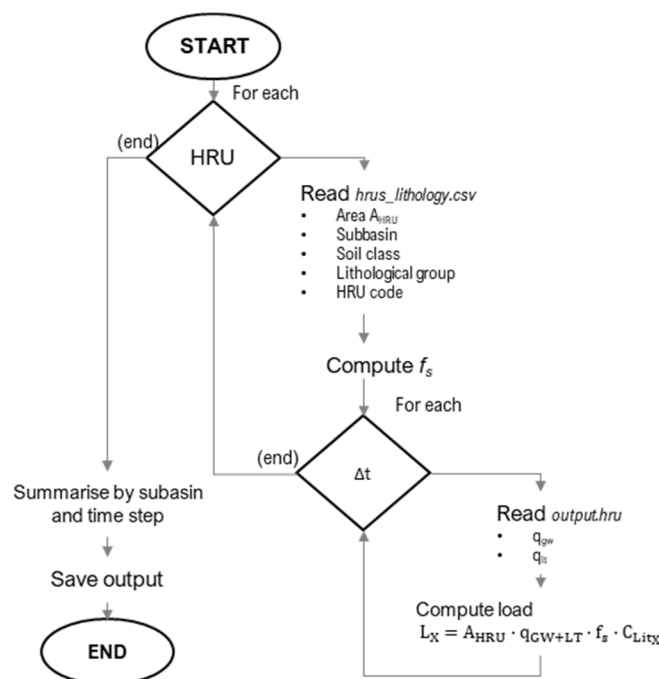
133 Once a QSWATLitho project has been set up, the calibration of the hydrology is needed, since this is the main  
134 dynamic input data for the ICWR model. Because the chemical weathering process occurs mainly in the  
135 vadose zone of the water cycle, the main water fluxes to be considered are groundwater ( $q_{gw}$ ) and lateral flows  
136 ( $q_{lf}$ ). The ICWR model has been adapted to include them ( $q_{lf}+q_{gw}$ ) instead of the total average specific  
137 discharge ( $q_{am}$ ), which would also include runoff. Here, the runoff is considered as the main driver for the  
138 dilution of the total load rather than including it in the calculation of the daily geochemical loads. A new  
139 module has been created so that the user can use the SWAT results, in combination with the QSWATLitho  
140 tables, to obtain geochemical loadings' daily time series. The module consists of six main steps that are  
141 integrated into two loops. For each HRU, data like area, lithological group, and soil type is extracted from the  
142 *hrus\_lithology.csv* file (a modified version of the *hrus* file in the *Project.mdb*) and, if necessary, used to set the  
143 soil shielding effect,  $f_{sx}$  (cf. [Lechuga-Crespo et al., 2020a](#)). Then, the *output.hru* file is read to obtain the  
144 specific discharge in the lateral and groundwater fluxes to the river. With this information, together with the  
145 globally fitted parameters, the geochemical loads are calculated for each time step of the simulation and each  
146 HRU. This process generates a table with the loads of each HRU to the river stream for each time step. Then,  
147 all of the loadings are summarised at the subbasin scale in each time step and saved as output. The  
148 geochemical loadings are routed by adding the upstream loadings (if such exists) to the contribution of each  
149 subbasin draining area. A workflow summary is shown in Figure 2, and the modified version of the ICWR  
150 regression (Equation 1) is shown in Equation 2, where  $L_x$  represents the loading of ion x in each HRU (in  
151  $Mg \cdot d^{-1}$ ),  $A$  is the area of the catchment in  $m^2$ ,  $q_{GW+LT}$  accounts for lateral and groundwater-specific discharge  
152 (mm), respectively,  $f_{sx}$  represents the soil shielding effect (dimensionless), and  $C_{Lit,x}$  is the globally fitted

153 parameter for each lithological unit and ion ( $\text{mol}\cdot\text{L}^{-1}$ ). Note that units are adjusted depending on the ion that is  
 154 being considered and that this modification considers each HRU to be a monolithic unit to the river stream.

155  $L_x = A_{HRU} \cdot (q_{GW+LT}) \cdot f_{s_x} \cdot C_{Lit_x}$  Equation 2

156 The lithological groups used in the ICWR model development study are kept unaltered in the present  
 157 development: evaporites (ev), metamorphics (mt), plutonic acid (pa), plutonic basic (pb), plutonic  
 158 intermediate (pi), pyroclastics (py), sediment carbonates (sc), sediment mixed (sm), sediment siliciclastic (ss),  
 159 sediment unconsolidated (su), volcanic acid (va), volcanic basic (vb), volcanic intermediate (vi), water bodies  
 160 (wb), ice and glaciers (ig), and no data (nd), according to the description presented in Hartmann and Moosdorf  
 161 (2012) and Dürr et al. (2005).

162



163 **Figure 2.** Workflow of the algorithm used to estimate the chemical weathering loadings from the outputs of the QSWATLitho project  
 164 calibrated for discharge. Ellipses indicate the start and end of the algorithm. The diamonds represent the loops: one for each HRU in  
 165 the project and another for each time step ( $\Delta t$ ) simulated (year, month, day). The arrows indicate the action sequence.

166 **2.3 Case study: Deba River catchment**

167 A case study is set up to explore the model's application. The validation comprises three steps: first, the  
 168 annual comparison of the results to evaluate the model's sensitivity and select the input data among different  
 169 combinations; second, the analysis of geochemical loadings in all subbasins derived from the QSWATLitho +  
 170 SWATLitho combination (spatial downscaling); and last, the comparison of the daily representation in three  
 171 gauging stations (temporal downscaling). The case study selected for this purpose is the Deba River catchment  
 172 (Figure 3), on which numerous studies related to urban and industrial pollution on its sediments and waters  
 173 have been conducted (Martínez-Santos et al., 2015; García-García et al., 2019; Unda-Calvo et al., 2019;  
 174 Lechuga-Crespo et al., 2020b). There are eleven sampling locations along its main channel and tributaries,

175 where a monitoring campaign was established between April 2014 and January 2017. Samples were taken in a  
176 monthly or bi-monthly time step. In addition, there are three gauging stations measuring, among other  
177 variables, discharge and electrical conductivity every 10 minutes.

### 178 2.3.1 Study area

179 The Deba River Basin has a complete drainage area of 538 km<sup>2</sup> and 60 km of main stream, a maximum slope  
180 of 40%, and an elevation varying from 0 at sea level to 1,320 m in Botreatiz (the highest mountain), which is  
181 located in the northern part of Spain, in the Gipuzkoa Province in the Basque Country (Figure 3). Regarding  
182 its hydrometeorology, there is a strong variation between humid and dry years, as well as a strong seasonal  
183 variability: about 30% of the total annual water volume is exported in December and January, and in dry  
184 summers, the specific discharge can reach 0.6 mm. The average annual precipitation is estimated to be 1,613  
185 mm, while the mean temperature is 12.7°C, leading to the highest potential evapotranspiration (ETP) of the  
186 surrounding catchments at 871 mm. In terms of the occupation of this catchment, there is a strong presence of  
187 industries, with a population of 135 000 inhabitants grouped into four important villages (Arrasate, Oñati,  
188 Bergara, Eibar, and Deba); 37% of the area is occupied by *Pinus spp*; 27% is covered by autochthonous forest,  
189 and 11% is given to farmlands and pastures. This catchment is commonly located over evaporitic rocks  
190 (gypsum and anhydrite deposits) included in detrital rocks, which, according to the classification proposed by  
191 Hartmann and Moosdorf (2012) and Dürr et al. (2005), correspond to a mix of siliciclastic, carbonate and  
192 mixed sediments, together with other lithological groups. A detailed description of the geology of the zone is  
193 addressed in Ábalos et al. (2008) and Iribar and Ábalos (2011). Historically, this catchment has suffered a  
194 strong urban and industrial pressure (Gipuzkoa Council, accessed on October 2019), and previous studies on  
195 the pollution in this catchment (Martínez-Santos et al., 2015; García-García et al., 2019; Unda-Calvo et al.,  
196 2019) have highlighted the inputs of urban and (residual) industrial effluents treated through wastewater  
197 treatment plants (WWTP) located in the middle of the catchment, where phosphorus is eliminated using Cl<sub>3</sub>Fe  
198 (only from May 1<sup>st</sup> to October 15<sup>th</sup>), resulting in the presence of metals in the water and sediment matrixes.  
199 The analysis of this anthropogenic influence has been monitored from April 2014 to January 2017 in 11  
200 sampling locations in the main channel and tributaries, highlighting the nutrients and metal input of urban and  
201 industrial effluents. Furthermore, a recent study on this catchment has focused on the major ion chemistry of  
202 its waters, assessing the main geochemical processes input in relation to the anthropogenic input (Lechuga-  
203 Crespo et al., 2020b) while emphasising the influence of an evaporitic saline spring in the southwest part of  
204 the catchment, which exerts a great impact on the water chemistry downstream to the outlet of the catchment.

### 205 2.3.2 Set up of the QSWATLitho project

206 A local Digital Elevation Map (DEM, 25m resolution cell) was used to create the stream network, locate the  
207 outlet of the catchment, and delimit the drainage area. Subbasins were merged to obtain their draining to the  
208 sampling locations of the monitoring campaigns. A European land use map from the CORINE Land Cover  
209 project (100m resolution), a soil map from the Harmonized World Database (a 30 arc-second resolution), and



210 a local lithological map reclassified for the categories found in Hartmann and Moosdorf (2012) were  
 211 combined with the DEM-derived slope map to create the HRUs (the description and source of the datasets  
 212 may be seen in Table 1, Table 2, and Figure 3). While setting up the model, three slope ranges were  
 213 established (0%-5%, 5%-10%, >10%) and no simplification was performed to reduce the number of HRUs.  
 214 The weather input data was obtained from a hydrometeorological station located close to the outlet (Figure 3),  
 215 consisting of precipitation as well as maximum and minimum temperature daily time series from January  
 216 1994 to December 2017. The observed data for discharge was covered from January 2004 to December 2017  
 217 for three gauging stations located close to the outlet and near the outlet of the two major subbasins of this  
 218 catchment (see Figure 3). SWAT has been used to compute the hydrological representation of the case study,  
 219 using the QSWATLitho HRU definition for the spatial discretization, but using the same water balance as the  
 220 SWAT model.

221 Observed data for riverine chemical concentration ranged from April 2014 to January 2017. A monitoring  
 222 program samples the river waters monthly or bimonthly using a pre-washed polypropylene bottle which was  
 223 carried to the laboratory at 4°C and filtered through 0.45µm filters. One replicate was acidified to 0.2% with  
 224 HNO<sub>3</sub> (68%) for base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) using ICP-OES (Perkin Elmer Optima 2000). The  
 225 other non-acidified replicate was used to analyse anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) through ion chromatography  
 226 (DIONEX ICS 3000). Alkalinity was measured using a Total Organic Carbon Analyzer (TOC-L Shimadzu).  
 227 The ionic charge balance (ICB) was within ±10% for all samples used in this study. For the modelling of the  
 228 geochemical loads, groundwater and lateral flows from the SWAT hydrological representation have been used  
 229 as a source of lithological chemical weathering derived loads, while runoff has been attributed to lower  
 230 concentrations, inducing dilution in the stream's concentration.

231 Following the recommendations of ASABE (2017), three periods were defined in this project: a warmup  
 232 period to reduce the effect of state variables' initial values (six years, January 1998-December 2003), a  
 233 calibration period to optimise the parameters (ten years, January 2004-December 2013), and a validation  
 234 period to test the model capabilities in an independent dataset (four years, January 2014-December 2017). The  
 235 model's performance evaluation has been carried out for the calibration and validation periods independently,  
 236 using graphical methods (time series between observed and simulated), and relative statistical measures  
 237 (coefficient of determination, r<sup>2</sup>, Nash-Sutcliffe Efficiency, NSE, PBIAS, and Kling-Gupta, KGE). The  
 238 Moriasi et al. (2015) standard has been considered in this study to evaluate the model's performance.  
 239 However, the authors have found no reference when comparing the daily loads of major ions, so the  
 240 exploration of the results would yield the first reference for future similar analysis.

241 **Table 1.** Input data type, description and sources for the case study set up project used in the present study.

| Input Data                    | Type   | Description   | Source            |
|-------------------------------|--------|---|-------------------|
| Digital Elevation Model (DEM) | Raster | A raster representing the elevations at 25x25m resolution | www.geouskadi.eus |

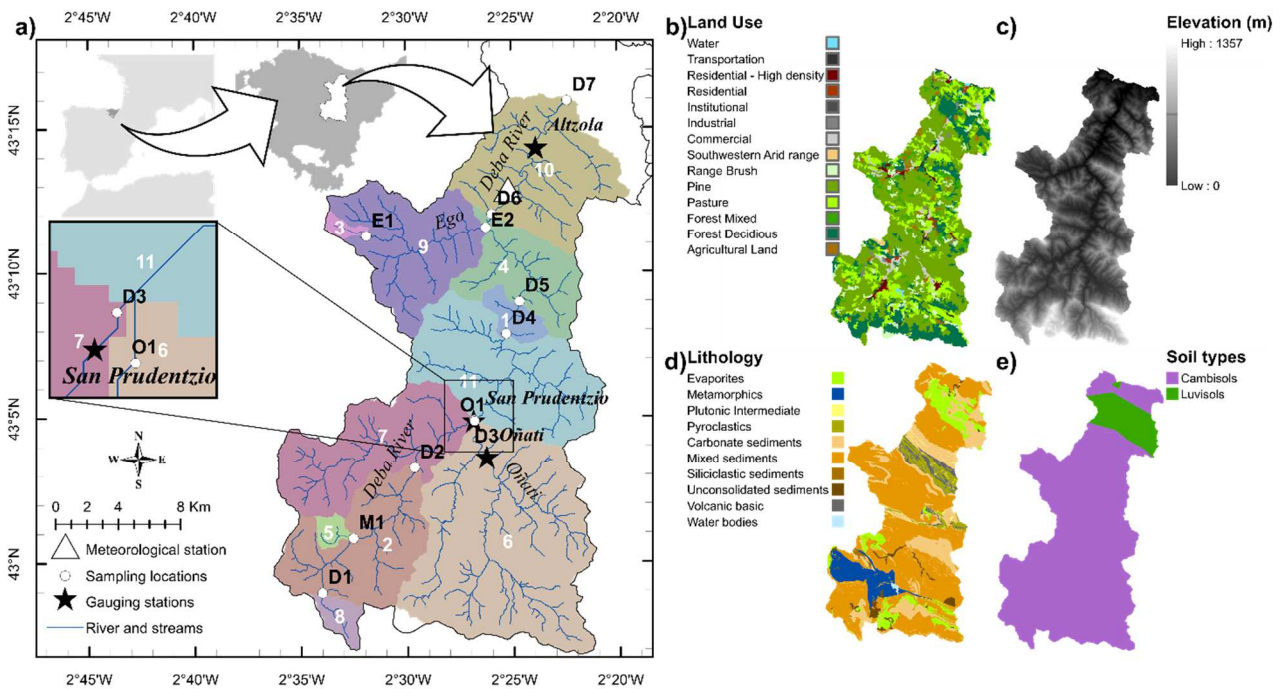
|                               |           |  |   |
|-------------------------------|-----------|--|---|
| Land Use                      | Raster    | A raster representing the land uses of the catchment, at a resolution of 100x100m    | <a href="https://land.copernicus.eu/pan-european/corine-land-cover">https://land.copernicus.eu/pan-european/corine-land-cover</a>   |
| Soil Type                     | Raster    | A raster representing the main types of catchment soil                               | <a href="http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/index.html?sb=1">http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/index.html?sb=1</a> |
| Lithology                     | Raster    | A derived raster representing the lithological classes of the catchment              | <a href="http://www.geoeuskadi.eus">www.geoeuskadi.eus</a>  |
| Precipitation and Temperature | Text File | Time series at one station with daily precipitation, maximum and minimum temperature | Spanish Agency of Meteorology (AEMET)   |

242 **Table 2.** Lithological distribution of the Deba River basin and its subbasins. Data derived from the Lithological Map of Euskadi  
 243 (www.geoeuskadi.eus), reclassified for Hartmann and Moorsdorf's (2012) lithological categories. Original map and lithological  
 244 classification are available in Supplementary Information (Figure S1 and Table S1).

| Lithology               | Main channel |      |       |       |       |       |       | Tributaries |       |     |      |
|-------------------------|--------------|------|-------|-------|-------|-------|-------|-------------|-------|-----|------|
|                         | D1           | D2   | D3    | D4    | D5    | D6    | D7    | M1          | O1    | E1  | E2   |
| Area [km <sup>2</sup> ] | 6.2          | 62.4 | 121.1 | 321.0 | 329.2 | 419.0 | 485.7 | 3.5         | 129.6 | 2.4 | 55.5 |
| ev                      | 4%           | 3%   | 7%    | 7%    | 7%    | 6%    | 7%    |             | 11%   |     |      |
| mt                      |              | 25%  | 27%   | 11%   | 11%   | 9%    | 7%    |             | 3%    |     |      |
| pi                      |              |      |       |       |       |       | 1%    |             |       |     |      |
| py                      |              |      |       | 2%    | 2%    | 5%    | 5%    |             |       |     | 5%   |
| sc                      | 19%          | 11%  | 9%    | 16%   | 16%   | 15%   | 18%   | 3%          | 18%   | 2%  | 14%  |
| sm                      | 77%          | 54%  | 51%   | 60%   | 61%   | 61%   | 58%   | 97%         | 66%   | 98% | 78%  |
| ss                      |              | 1%   | 1%    | 1%    | 1%    |       |       |             |       |     |      |
| su                      |              | 6%   | 5%    | 3%    | 3%    | 2%    | 2%    |             | 3%    |     |      |
| vb                      |              |      |       | 1%    | 1%    | 2%    | 3%    |             |       |     | 3%   |
| wb                      |              |      |       |       |       |       |       |             | 1%    |     |      |

Lithological classes: evaporites (ev), metamorphics (mt), plutonic intermediate (pi), pyroclastics (py), carbonate sediments (sc), mixed sediments (sm), siliciclastic sediments (ss), unconsolidated sediments (su), volcanic basic (vb), water bodies (wb)

245



246

247 **Figure 3.** Deba River catchment description: a) localisation, main channel and tributaries, sampling locations, gauging stations and  
 248 subbasins used in the present study; b) land use; c) digital elevation map; d) lithological units; e) soil types. Figures b), c), d), and e)  
 249 are used for the setup of the model.

### 250 2.3.3 Discharge parameterisation

251 The geochemical reactions responsible for ionic loads derived from rocks to the river are assumed to be in  
 252 equilibrium at daily scales; however, other sources like human input or atmospheric deposition are expected to  
 253 vary in these temporal ranges. Thus, the simulation (both calibration and validation) has been done at a daily  
 254 time step. The first step is to calibrate the discharge (in surface runoff, lateral flow, and groundwater flow),  
 255 which will be the main drivers in the temporal application of the ICWR model. The discharge has been  
 256 calibrated using the parameters found in Table 3, through both manual calibration and autocalibration with the  
 257 SUFI-2 algorithm in SWAT-CUP (Abbaspour et al., 2007). Three gauging stations have been used to evaluate  
 258 the model performance on discharge calibration using four statistical criteria: the coefficient of determination  
 259 ( $r^2$ ), the Nash & Sutcliff Efficiency (NSE), the percent of bias (PBIAS), and the Kling-Gupta efficiency  
 260 (KGE). All the statistics are applied to the simulated and observed values:  $r^2$  focuses in the fit between the  
 261 trends, varying from 0 (no fit) to 1 (perfect fit); PBIAS calculates the global over- (negative value) or  
 262 underestimation (positive value); NSE evaluates the trends (similar to  $r^2$ , but varying from  $-\infty$  to 1, perfect fit);  
 263 and KGE is based on Pearson's coefficient "r", including bias and variability, ranging from  $-\infty$  to 1 (perfect  
 264 fit), where values  $> -0.41$  could be considered as a reasonable performance (Knoben et al. 2019).

265 **Table 3.** Parameters modified for calibration, type of change (v: value change, r: relative change), description and change adopted.

| File | Change type | Parameter name | Description   | Best fit | Minimum | Maximum |
|------|-------------|----------------|---|----------|---------|---------|
| gw   | v           | GW_DELAY       | Groundwater delay time  | 240.5    | 200     | 500     |
|      | v           | ALPHA_BF       | Baseflow alpha factor   | 0.27     | 0.05    | 0.3     |
|      | v           | GWQMN          | Threshold depth of water in shallow aquifer required for return flow to occur | 1081     | 600     | 1500    |
| hru  | v           | LAT_TTIME      | Lateral flow travel time  | 3.31     | 1       | 7       |
|      | r           | HRU_SLP        | Average HRU slope   | ↓15%     | ↓30%    | 0       |
|      | v           | CANMX          | Maximum canopy storage  | 17.8     | 5       | 20      |
| mgt  | r           | CN2            | Curve number for moisture condition II  | ↓26%     | ↓30%    | 0       |
| sol  | r           | SOL_AWC        | Available water capacity  | ↓11%     | ↓20%    | ↑30%    |
|      | r           | SOL_K          | Soil hydraulic conductivity   | ↑5%      | -       | ↑30%    |

266

### 267 2.3.4 Downscaling the ICWR model

268 The original ICWR model (Lechuga-Crespo et al., 2020a) was developed for an annual average specific flux  
 269 output for which only the average specific discharge was needed for hydrology. To explore the possibilities of  
 270 applying this model at lower spatial and temporal scales, three assessments have been performed: a model's  
 271 sensitivity analysis, a spatial evaluation, and a temporal assessment. The model's sensitivity to input data was  
 272 evaluated by testing different global and local datasets combinations. Two lithological maps, one clipped from  
 273 the Global Lithological Map (GLiM, Hartmann and Moosdorf, 2012), and a local one obtained from the  
 274 Gipuzkoa Council (geoeskadi.eus), together with two annual average specific discharges, one obtained from  
 275 a global dataset (UNH/GRD, Fekete et al., 2002) and other from the Gipuzkoa Council Hydrological  
 276 Department (www.gipuzkoa.eus), were combined to obtain four output datasets. The comparison with  
 277 observed data indicated the best input data setup for building the QSWATLitho project. These results are

278 shown and discussed in section 3.1.1 *Model's sensitivity to input data*. Before applying the SWATLitho  
279 module, it is necessary to calibrate the water balance. The model setup and the calibration of hydrology are  
280 discussed in section 3.1.2 *Case study*. Once the model was built and hydrology was calibrated, a simulation  
281 was conducted (period: January 2014 to December 2017). The application of the SWATLitho module allowed  
282 the evaluation of the model's spatial and temporal performance. No calibration of the ICWR parameters has  
283 been done, and globally fitted values were used (Lechuga-Crespo et al., 2020a). The model's spatial  
284 downscaling evaluation was done by contrasting simulated geochemical loadings at the subbasin outlet with  
285 observed loadings at the corresponding sampling location (see Figure 3a). Results are presented in section  
286 3.1.3 *Spatial downscaling*. The temporal downscale was evaluated at three gauging stations, where daily  
287 loadings were derived from punctual data and continuous registries integration. The results are shown in  
288 section 3.1.4 *Temporal downscaling*. Finally, model limitations, improvement suggestions, and alternatives  
289 are presented in section 3.1.5 *SWATLitho limitations and alternatives*. Even though the wide applicability of  
290 the model makes this approach versatile, its setup may be constrained by input data availability.

291 A proposed alternative approach is the use of digital filters to deconvolute the hydrological signal between  
292 surface and groundwater fluxes. In this sense, we computed the hydrological deconvolution using the  
293 Eckhardt digital filter (Eckhardt 2005; Xie et al., 2020). This test has been performed at the three gauging  
294 stations of the catchment.

## 295 **3 Results and discussion**

### 296 *3.1.1 Model's sensitivity to input data*

297 Average annual loadings obtained for the four input data combinations are shown in Table 4. The original  
298 ICWR model (Lechuga-Crespo et al., 2020a) was calibrated and validated using global data (method  
299 UNH+GLIM in Table 4) and data on rivers worldwide from the GLORICH database. The highest values  
300 among all methods considered are found for the UNH+GLIM method, and the greatest differences are found  
301 not between the two hydrological datasets but between the lithological maps. This confirms that the  
302 lithological representation has a major impact on the loadings computed by the model. Regarding the values  
303 obtained with the four datasets in comparison with the observed values (Gauging station in Table 4), the  
304 closest values are found for the EUS+GEUS method, the local data for hydrology and lithology. Nevertheless,  
305 the difference between the observed and the modelled values are different between ions and gauging stations.  
306 Both the Altzola and San Prudentzio gauging stations present the highest differences in  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$ ,  
307 while the differences between the observed and the simulated values are lower for other ions. Such differences  
308 are not found in the Oñati tributary, where the highest difference is found for  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ , but which  
309 is still lower than the Altzola and the San Prudentzio bias for the previously noted ions. The common pattern  
310 in the differences found for Altzola and San Prudentzio and the difference for the Oñati stream suggest that

311 there is a common phenomenon not captured by the model's performance in the San Prudentzio draining  
 312 basin, which affects downstream at the outlet of the catchment.

313 The monitoring program and previous studies in the area (Iribar and Ábalos 2011; Martínez-Santos et al.,  
 314 2015) have shown that the southeastern part of the catchment has the highest values of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ ,  
 315 which is related to the presence of gypsum intrusions and a spring, altering the local water's composition. In  
 316 both lithological maps used, the intrusion of gypsum (evaporites) in the southwest part of the catchment seems  
 317 to be underestimated. In addition, according to Iribar and Ábalos (2011), the southern part of the catchment  
 318 contains a combination of different geological registries (Albian and Aptian-Albian) where there is a common  
 319 presence of springs with saline waters. Within this catchment, the Leintz-Gatzaga spring contains one of the  
 320 most concentrated effluents to the streams ( $230.6 \text{ g}\cdot\text{L}^{-1}$  according to Iribar and Ábalos, 2011). This suggests  
 321 that the impact of the saline is not properly mapped in either the global or the local lithological maps, but that  
 322 it exerts a strong influence on the chemical characteristics of this area downstream (Lechuga-Crespo et al.,  
 323 2020b). For this reason, the observed data on  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  are higher than those modelled, especially in the  
 324 San Prudentzio subbasin. The inclusion of a local lithological map, with a finer spatial resolution of lithology,  
 325 has decreased the loads to around half of those obtained with the previous map. These new values are closer to  
 326 reality when considering  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$ , which are the elements less affected by the spring inputs.  
 327 The inclusion of a spatially distributed lithology has improved the results of the model, leading to the  
 328 conclusion that increasing the spatial resolution of the lithology input data has a major effect on the output of  
 329 the model.

330 From the model's sensitivity analysis, we conclude that when applying the ICWR model to local studies, local  
 331 lithological data should be applied. Moreover, consideration of saline springs should be taken into account  
 332 when evaluating the model's performance.

333 **Table 4.** The table demonstrates the average annual loadings that were obtained using the ICWR model in the Deba River catchment,  
 334 with different input data. UNH represents the global hydrological dataset (UNH/GRDC, Fekete et al., 2002), the EUS indicates the  
 335 local average data from the Gipuzkoa Council Hydrological Department (www.gipuzkoa.eus), the GLIM denotes the global  
 336 lithological map (GLIM, Hartmann and Moosdorf, 2012), the GEUS implies the local lithological map (www.geoeuskadi.eus),  
 337 Gauging station represents the data obtained from each gauging station. All values expressed as mean annual load in  $[\text{Mg}\cdot\text{y}^{-1}]$ .

| Method          | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{Cl}^-$ | $\text{HCO}_3^-$ | $\text{SO}_4^{2-}$ |
|-----------------|------------------|------------------|---------------|--------------|---------------|------------------|--------------------|
| <i>Altzola</i>  |                  |                  |               |              |               |                  |                    |
| UNH+GLIM        | 24783            | 5923             | 3707          | 755          | 6675          | 104465           | 20457              |
| EUS+GLIM        | 22393            | 5352             | 3349          | 682          | 6031          | 94389            | 18484              |
| UNH+GEUS        | 10492            | 2262             | 1991          | 348          | 3272          | 45897            | 14792              |
| EUS+GEUS        | 9480             | 2044             | 1799          | 314          | 2957          | 41470            | 13365              |
| Gauging station | 20777            | 1755             | 6358          | 1050         | 10485         | 55244            | 14513              |
| <i>Oñati</i>    |                  |                  |               |              |               |                  |                    |
| UNH+GLIM        | 6918             | 1651             | 1019          | 210          | 1842          | 28922            | 5640               |
| EUS+GLIM        | 7233             | 1726             | 1066          | 220          | 1926          | 30238            | 5897               |
| UNH+GEUS        | 2852             | 589              | 525           | 78           | 881           | 12565            | 4152               |
| EUS+GEUS        | 2981             | 616              | 549           | 82           | 921           | 13137            | 4341               |

|                       |      |      |      |     |      |       |      |
|-----------------------|------|------|------|-----|------|-------|------|
| Gauging station       | 3894 | 294  | 314  | 84  | 381  | 10918 | 1861 |
| <i>San Prudentzio</i> |      |      |      |     |      |       |      |
| UNH+GLIM              | 5353 | 1287 | 861  | 164 | 1513 | 23340 | 4646 |
| EUS+GLIM              | 4237 | 1019 | 681  | 130 | 1198 | 18473 | 3677 |
| UNH+GEUS              | 2034 | 416  | 384  | 70  | 642  | 8871  | 2971 |
| EUS+GEUS              | 1610 | 330  | 304  | 56  | 508  | 7021  | 2351 |
| Gauging station       | 5691 | 497  | 2526 | 394 | 4266 | 14865 | 4381 |

338

### 339 3.1.2 Case study set-up and discharge calibration

340 The combination of slope, land use, soil types, and lithological classes in this catchment leads to a spatial  
341 discretisation consisting of 11 subbasins and 985 HRUs. When building the same project considering land use,  
342 soil type, and slope layers in the HRU definition step, the number of spatial units reaches 286 HRUs. A more  
343 detailed project regarding spatial distribution increases the computation time, but the water balance calibration  
344 is more comprehensive, which is a key input for the geochemical loads' computation, and the model's  
345 temporal downscaling.

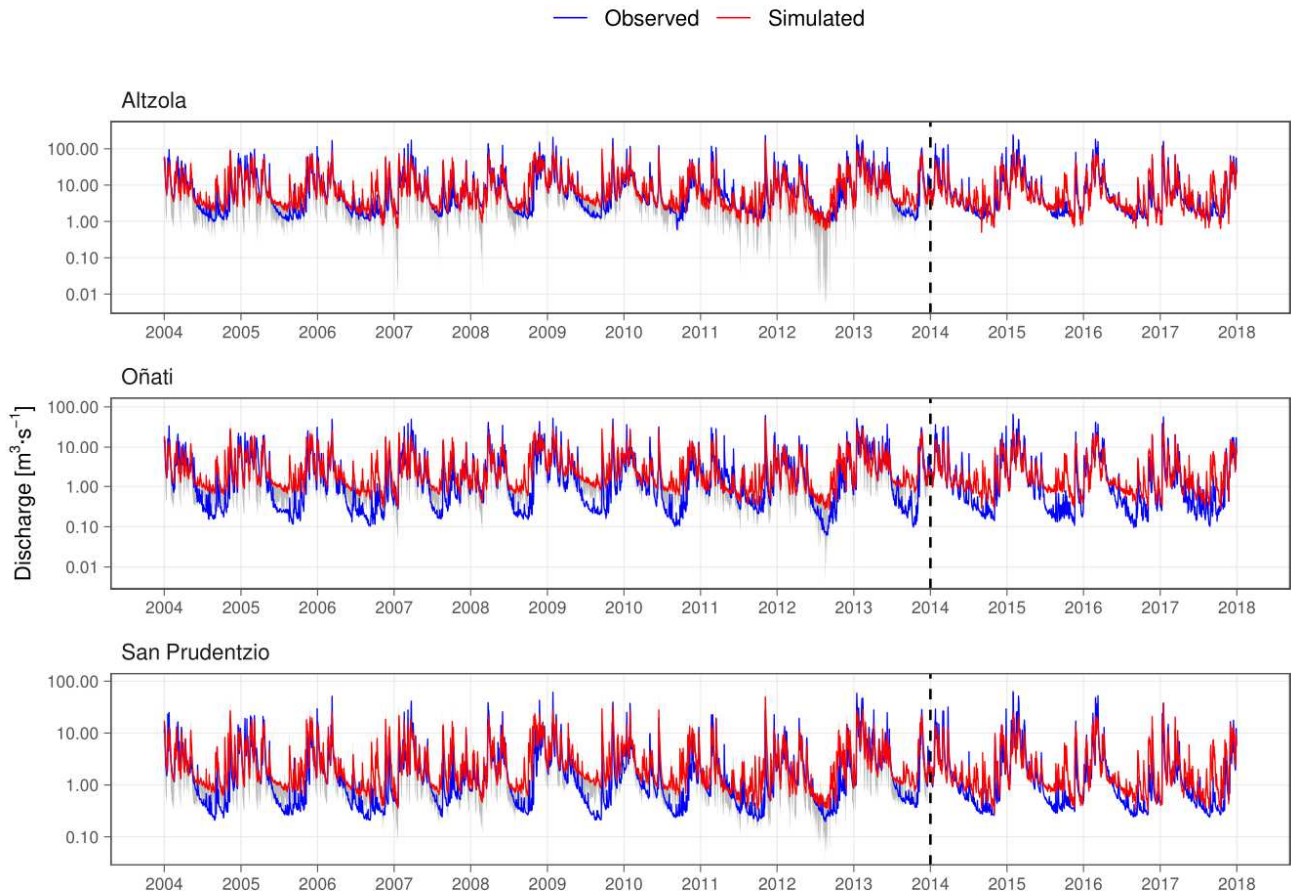
346 Regarding the calibration of hydrology at the daily time step (Figure 4), most of the parameterisation has been  
347 focused on calibrating groundwater and lateral flow, which account for almost 96% of the annual discharge at  
348 the catchment's outlet. The parameterisation of the model has yielded the results summarised in Table 5, and  
349 Moriasi et al. (2015) qualifies the simulation as "Satisfactory" for calibration and validation. According to  
350 these results, the model has been considered enough to represent the hydrology of the catchment studied.

351 NSE is used based on its performance, which is better when the variable's range of variation is large.  
352 However, in low flows, the denominator tends towards 0, leading to higher values when the errors are small  
353 (Oeurng et al., 2011). The higher values for  $r^2$  in comparison to the NSE suggest a good representation of the  
354 dynamic, but a worse depiction of the exact discharge value, indicating a difference between observed and  
355 simulated values which is stronger in lower flow periods. This can also be seen in the PBIAS, where the  
356 calibration for San Prudentzio has yielded a value classified as "Non-Satisfactory" according to Moriasi et al.  
357 (2015). A negative value of the PBIAS proposes an underestimation of the model, which is attributed to peaks  
358 in the drier period of the simulation. Fluctuations are related to the way groundwater is calculated in SWAT,  
359 not using a spatially diffused flow, but pulses in each HRU (Bailey et al., 2019). Improvements in the model  
360 performance for hydrology may be expected by incorporating a more detailed soil map, as the present  
361 resolution seems too coarse for the needs of this modelling.

362 The most sensible parameters are the SCS curve number (CN2.mgt), which was decreased to adjust the peak  
363 discharge in combination with the maximum canopy storage (CANMX.hru), the baseflow recession constant  
364 (ALPHA\_BF.gw) and the lateral flow travel time (LAT\_TTIME.hru).The lateral flow has a relevant role in  
365 the hydrology of this catchment. Baseflow was adjusted using the delay of water passing through the last soil

366 layer (GWDELAY.gw) and the water threshold in the shallow aquifer needed for groundwater flow to occur  
 367 (GWQMIN.gw). All specific changes are shown in Table 3.

368



369

370 **Figure 4.** Time series of daily simulation and observation discharge in three sampling locations in the catchment. A dashed line  
 371 separates the calibration from the validation period. The grey band in the calibration period represents the 95<sup>th</sup> lower and upper limits  
 372 of the 100 simulations performed using the SUFI2 algorithm in SWATCUP (Abbaspour et al., 2007, 2014). As there is a relevant  
 373 difference in discharge ranges between the dry and the wet periods, the vertical axis is plotted in logarithmic scale.

374 **Table 5.** Summary of hydrological calibration and validation in three gauging stations at a daily time step.  $r^2$  represents the coefficient  
 375 of determination, where 0 = no correlation and 1 = perfect fit; NSE is the Nash-Sutcliffe Efficiency, where  $< 0$  = observed mean better  
 376 than simulation, 0 = model prediction is accurate as observed mean, and 1 = perfect fit; PBIAS represents the tendency of the  
 377 simulation to be larger or smaller than the observations, where  $> 0$  = overestimation of the model,  $< 0$  = underestimation of the model,  
 378 KGE is the Kling-Gupta Efficiency, where values  $> -0.41$  are considered as reasonable (Kobne et al., 2019), and 1 = perfect fit.  $P$ -  
 379 factor represents the fraction of the measured data falling within the 95% prediction uncertainty band, while  $r$ -factor is the ratio of the  
 380 average width of the band and the standard deviation of the measured variable.

|                | Calibration                  |      |           |      |          | Validation                   |       |      |           |      |
|----------------|------------------------------|------|-----------|------|----------|------------------------------|-------|------|-----------|------|
|                | January 2004 - December 2013 |      |           |      |          | January 2014 - December 2017 |       |      |           |      |
|                | $r^2$                        | NSE  | PBIAS (%) | KGE  | p-factor | r-factor                     | $r^2$ | NSE  | PBIAS (%) | KGE  |
| Altzola        | 0.72                         | 0.71 | -0.7      | 0.71 | 0.65     | 0.42                         | 0.76  | 0.68 | 13.7      | 0.56 |
| Oñati          | 0.64                         | 0.64 | -13.5     | 0.71 | 0.47     | 0.48                         | 0.74  | 0.71 | 0.9       | 0.64 |
| San Prudentzio | 0.65                         | 0.62 | -28.4     | 0.64 | 0.57     | 0.5                          | 0.7   | 0.66 | -4.8      | 0.60 |

381

382

### 383 *3.1.3 Spatial downscaling*

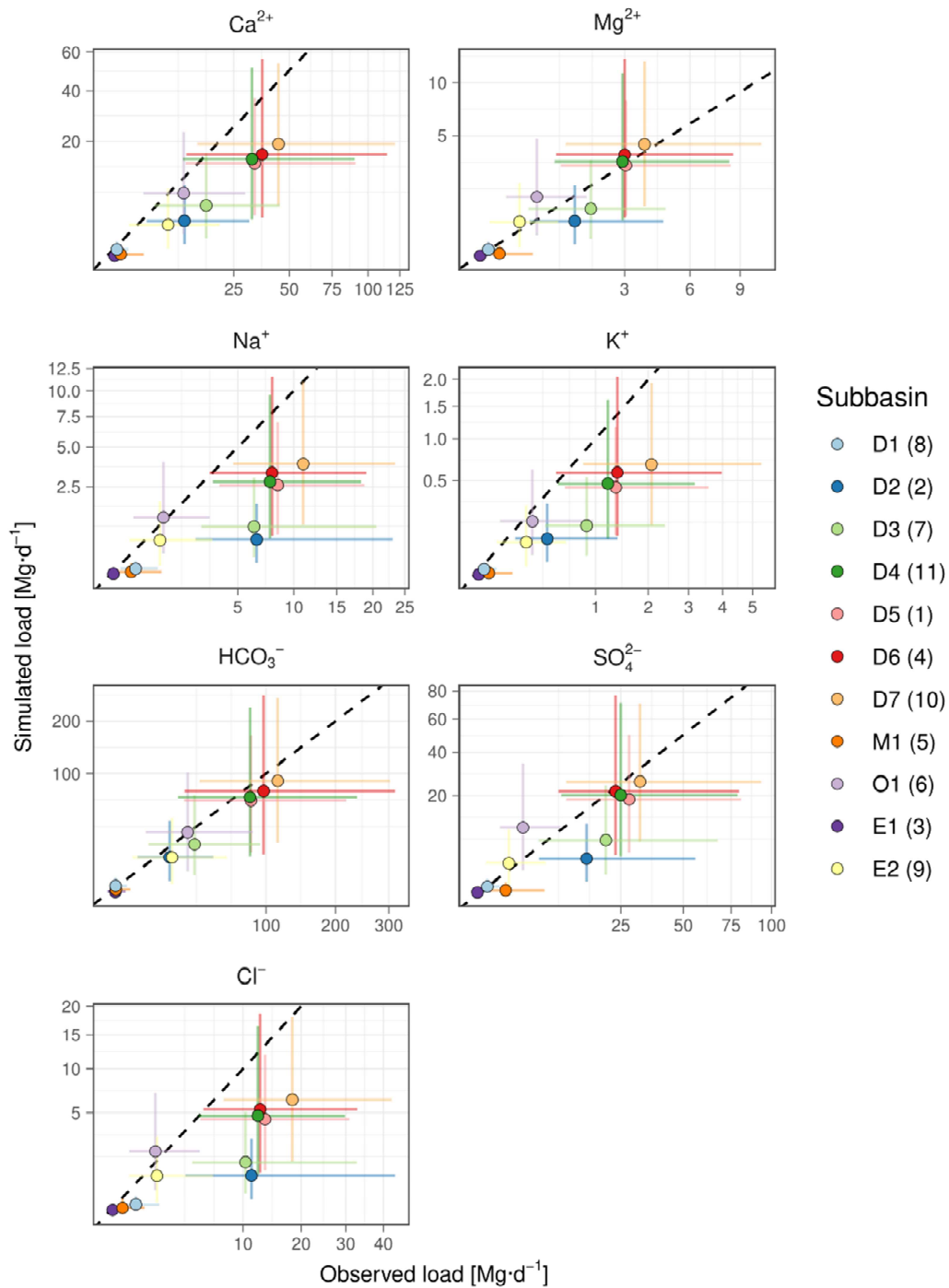
384 The geochemical loadings derived from rock's chemical weathering are carried out by the rivers to oceans and  
385 lakes. Disregarding instream transformation (outgassing, biological uptake, secondary precipitation, or ionic  
386 exchange processes) loadings are added along the river network. Figure 5 presents the comparison of these  
387 loadings at the outlet of each subbasin, which has a corresponding sampling location. Only fluxes from  
388 sampling campaigns are considered (cf. Lechuga-Crespo et al., 2020b). As expected, there is a corresponding  
389 generally increasing trend between the two signals. Downstream sampling locations have higher exports than  
390 upstream subbasins. However, the trend is different for each ion.

391  $Mg^{2+}$ ,  $SO_4^{2-}$ , and  $HCO_3^-$  present the best spatial collinearity among all ions, and the mean loadings in each  
392 sampling location are scattered around the perfect fit line. The largest deviations are  $Na^+$  and  $Cl^-$ , where  
393 observed values are higher than the simulation ones. Nevertheless, since loadings are added through the  
394 routing network, upstream errors are carried downstream. Specific attention to the D2 and D3 sampling  
395 locations (subbasins 2 and 7, respectively) indicate underestimation for all ions, especially  $Na^+$  and  $Cl^-$ . This  
396 suggests that this area contains an ionic point source loaded with these ions, which is not captured by the  
397 model. This results in the worst representation among all of the catchments.

398 Among the headwater sampling locations (D1, E1, M1, and O1) and subbasins (8, 3, 5, and 6, respectively),  
399 the Oñati stream presents the largest loadings, in which ions are commonly located close to the perfect fit line  
400 except for  $Mg^{2+}$  and  $SO_4^{2-}$ . This overestimation compensates for the underestimation found in D3 for these  
401 ions, improving the overall representation of the model. Further analysis of this stream's temporal evolution is  
402 found in section *3.1.4 Temporal downscaling*.

403 The application of the model to this case study supports that headwater locations present lower discrepancies  
404 than downstream subbasins. This spatial analysis indicates that point sources exert a great impact on the  
405 model's performance, since downstream locations are conditioned by incoming loadings.





406

407 **Figure 5.** Simulated versus observed loadings for all sampling locations (subbasin number presented between  
 408 brackets). The point represents the mean value for the daily loadings, considering only dates with *in-situ*  
 409 monitoring campaigns. Horizontal and vertical lines present minimum and maximum values for observed and  
 410 simulated loadings.

#### 411 3.1.4 Temporal downscaling

412 Figure 5 presents a graphical assessment of the SWATLitho performance, comparing the simulated and  
 413 observed time series at three gauging stations (Alzola, San Prudentzio, and Oñati, Figure 3a). A visual

414 evaluation shows that the global fitted parameters applied to the calibrated QSWATLitho project yield  
415 geochemical loads showing a varying degree of similarity between the simulated and the observed values,  
416 suggesting the model performs differently depending on the ion and drainage basin being considered. Besides,  
417 Table 6 contains the statistical results for each pair of time series and the average values for each gauging  
418 station. Considering Altzola results as representative of the catchment-scale performance of the model, the  
419 average statistics show a reasonable performance from the model ( $r^2 = 0.74 \pm 0.02$ , PBIAS=-17.96  $\pm$  85.02,  
420 KGE=0.08  $\pm$  0.48), according to the criterion presented by Kobne et al. (2019) regarding KGE.

421 Focusing on the subbasin-scale, each mean statistic yields a different pattern for the model's performance. The  
422 mean coefficient of determination ( $r^2$ ) is comparable among gauging stations, suggesting that dynamic  
423 representation is homogeneous at the subbasin level. The mean percentage of deviation (PBIAS) indicates that  
424 the Altzola gauging station is the closest to reality, while Oñati presents the largest discrepancies; the Kling-  
425 Gupta Efficiency factor (KGE), as a summary statistic, is best for San Prudentzio and worst for Oñati.  
426 However, the analysis of the standard deviation highlights the presence of two outliers in Oñati:  $Mg^{2+}$  and  
427  $SO_4^{2-}$ . Excluding these outliers from the analysis yields the best values for Oñati in all statistics (KGE = 0.59  $\pm$   
428 0.19, PBIAS[%] = 13.22  $\pm$  34.68, and  $r^2 = 0.75 \pm 0.01$ ), and worst for San Prudentzio. The Altzola gauging  
429 station, which receives waters from Oñati, San Prudentzio and other tributaries in the main channel, presents  
430 intermediate statistics suggesting that the differences present in the upper part of the catchment are routed  
431 downstream to the outlet. This can also be seen in the times series in Figure 5, where the deviations between  
432 the observed and the simulated values are similar in Altzola and San Prudentzio, while they are independent at  
433 the Oñati stream. Using the KGE as an integrative measure of the model's performance, values  $>-0.41$  are  
434 considered reasonable (Kobne et al., 2019). This criterion yields a valid representation of the average ionic  
435 loadings in all gauging stations.

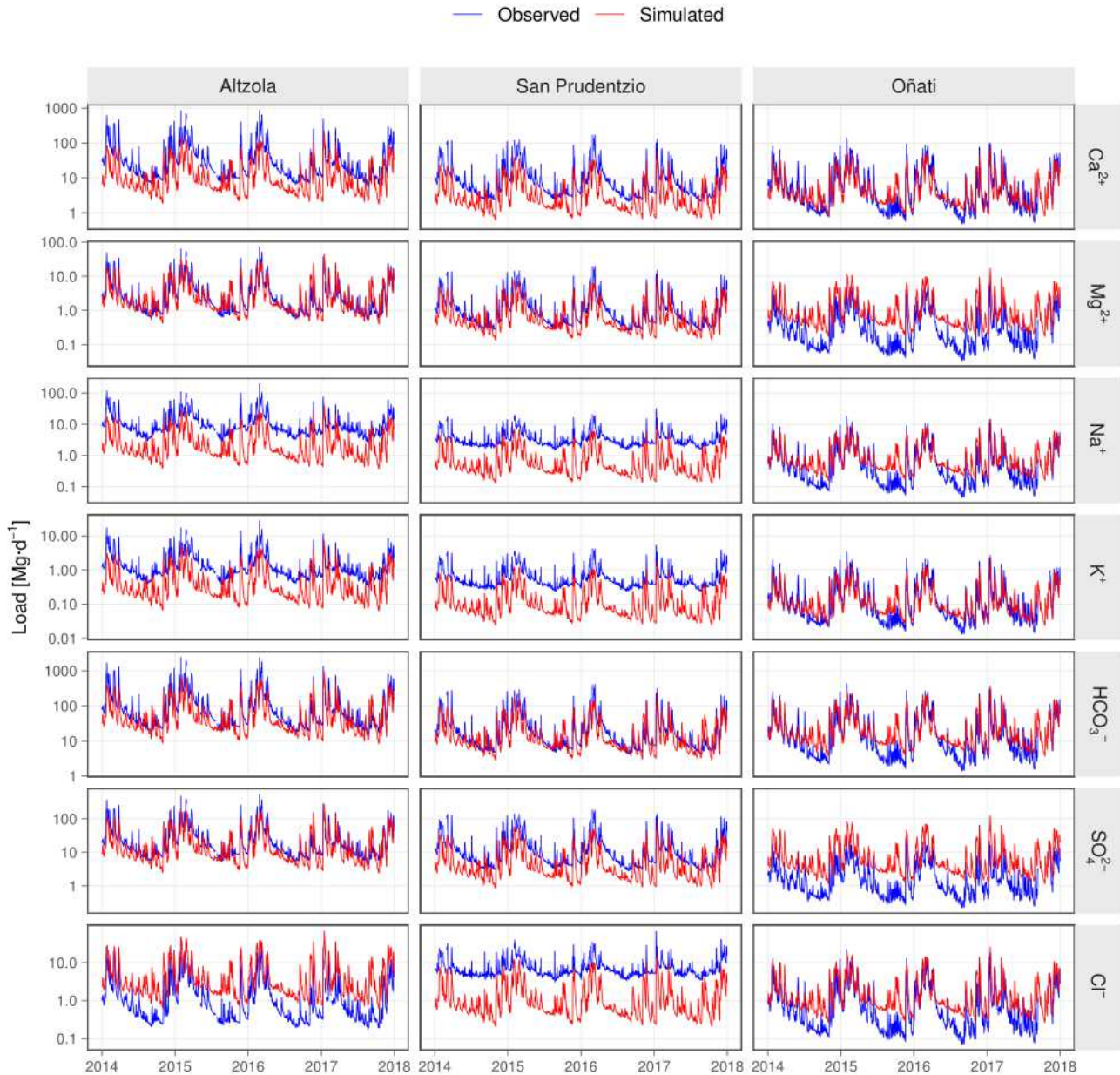
436 Previous studies in the area using *in-situ* samplings have highlighted the sulphate water composition in the  
437 Oñati stream of the catchment (Lechuga-Crespo et al., 2020b), which could be related to the evaporitic  
438 presence in the upper part of the catchment (Iribar and Ábalos, 2011). However, despite the evaporitic  
439 presence in the input data (largest percentage the in draining catchment, Table 2), a karstic presence has also  
440 been reported in the area (Iribar and Ábalos, 2011), which could be a source of diluted water to the system. A  
441 complex interaction of these saline and diluted water sources may be responsible for the discrepancies found  
442 between the simulated and the observed values for  $Mg^{2+}$  and  $SO_4^{2-}$ .

443 In addition, the presence of springs, i.e. wells with saline water, is common in the San Prudentzio stream  
444 (Iribar and Ábalos, 2011), particularly the Leintz-Gatzaga spring, which provides one of the most  
445 concentrated effluents, with 230.6 g·L<sup>-1</sup> of total dissolved solids and over 85 g·L<sup>-1</sup> of Cl<sup>-</sup> (Iribar and Ábalos,  
446 2011). The vertical pathway of this spring is over 384 m (Iribar and Ábalos, 2011), which explains the  
447 different dynamics of Cl<sup>-</sup>, Na<sup>+</sup>, and K<sup>+</sup> present in this area, as the input from the spring is steadier than the

448 rapid response of the groundwater and the lateral flow of the remaining catchment, changing the relative  
449 contribution of these ions to the total cation concentration with time ([Lechuga-Crespo et al., 2020b](#)).

450 There are few models similar to this one, but a recent publication ([Bailey et al., 2019](#)) introduced a saline  
451 module based on physical equations at chemical equilibrium into the SWAT code to analyse of the fate and  
452 transport of the ions in catchments. In addition, the researchers in that study reported problems of  
453 underestimation of the model's value regarding unmapped mineral presence in the input data, which also  
454 occurred in the present study. Both studies have shown the importance of measured concentrations in rivers as  
455 a proxy for the geochemical minerals affecting the riverine loads. In the present case, the monitoring  
456 campaigns, together with the gauging station's data, have recorded the effect of the spring input, which the  
457 model did not capture.

458



459

460 **Figure 6.** Time series (validation period: January 2014-December 2017) of daily simulated and observed loadings at three gauging  
 461 stations, Altzola, San Prudentzio, and Oñati, of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{HCO}_3^-$ . The gauging stations are located in the  
 462 outlet of the catchment and in two tributaries. Note that the vertical axis is in logarithmic scale to better differentiate the results in dry  
 463 and wet periods.

464 **Table 6.** Summary statistics for geochemical loadings in the Deba River urban catchment. The coefficient of determination is  
 465 represented by  $r^2$ , where 0 = no correlation, and 1 = perfect fit. NSE is the Nash-Sutcliffe Efficiency, where  $<0$  = observed mean better  
 466 than simulation, 0 = model prediction is accurate as observed mean, and 1 = perfect fit. PBIAS denotes the tendency of the simulation  
 467 to be larger or smaller than the observations, where  $>0$  = overestimation of the model, and  $<0$  = underestimation of the model. KGE is  
 468 the Kling-Gupta Efficiency, where values  $>-0.41$  are considered as reasonable (Kobne et al., 2019), and 1 = perfect fit. *mean* and *sd*  
 469 signify the arithmetic mean and standard deviation of all ions for each gauging station.

| Station | Ion              | $r^2$ | PBIAS [%] | KGE   |
|---------|------------------|-------|-----------|-------|
| Altzola | $\text{Ca}^{2+}$ | 0.76  | -67.70    | -0.02 |
|         | $\text{Mg}^{2+}$ | 0.76  | -9.80     | 0.68  |
|         | $\text{Na}^+$    | 0.70  | -73.90    | -0.04 |
|         | $\text{K}^+$     | 0.72  | -66.60    | 0.05  |
|         | $\text{HCO}_3^-$ | 0.75  | -44.30    | 0.26  |

|                |                               |      |        |       |
|----------------|-------------------------------|------|--------|-------|
|                | SO <sub>4</sub> <sup>2-</sup> | 0.76 | -31.10 | 0.46  |
|                | Cl <sup>-</sup>               | 0.73 | 167.70 | -0.84 |
|                | <i>mean</i>                   | 0.74 | -17.96 | 0.08  |
|                | <i>sd</i>                     | 0.02 | 85.02  | 0.48  |
| San Prudentzio | Ca <sup>2+</sup>              | 0.75 | -64.40 | 0.04  |
|                | Mg <sup>2+</sup>              | 0.75 | -38.40 | 0.38  |
|                | Na <sup>+</sup>               | 0.70 | -76.90 | 0.00  |
|                | K <sup>+</sup>                | 0.73 | -76.20 | -0.02 |
|                | HCO <sub>3</sub> <sup>-</sup> | 0.74 | -28.30 | 0.47  |
|                | SO <sub>4</sub> <sup>2-</sup> | 0.76 | -58.10 | 0.15  |
|                | Cl <sup>-</sup>               | 0.65 | -80.50 | -0.04 |
|                | <i>mean</i>                   | 0.73 | -60.40 | 0.14  |
|                | <i>sd</i>                     | 0.04 | 20.26  | 0.21  |
| Oñati          | Ca <sup>2+</sup>              | 0.74 | -23.00 | 0.55  |
|                | Mg <sup>2+</sup>              | 0.75 | 169.20 | -1.10 |
|                | Na <sup>+</sup>               | 0.75 | 25.40  | 0.70  |
|                | K <sup>+</sup>                | 0.75 | -13.80 | 0.64  |
|                | HCO <sub>3</sub> <sup>-</sup> | 0.75 | 13.10  | 0.79  |
|                | SO <sub>4</sub> <sup>2-</sup> | 0.67 | 284.30 | -2.90 |
|                | Cl <sup>-</sup>               | 0.75 | 64.40  | 0.29  |
|                | <i>mean</i>                   | 0.74 | 74.23  | -0.15 |
|                | <i>sd</i>                     | 0.03 | 112.97 | 1.38  |

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### 471 3.1.5 SWATLitho limitations and alternatives

472 A recent study has presented a physically-based module for assessing the fate and transport of saline ions in  
473 catchments integrated on the SWAT model (Bailey et al., 2019). That model has been developed to evaluate  
474 the best irrigation management practices and their impacts on the salinisation of freshwater environments  
475 within a catchment. The setup requirements are a discharge calibrated SWAT project, the initial  
476 concentrations of the ions in the soil and the aquifer, and the percentage of five solid species present in each  
477 HRU to compute the chemical equilibrium (Bailey et al., 2019). In contrast, the model introduced in the  
478 present study focuses solely on the process of chemical weathering. It computes the geochemical loadings  
479 derived from lithology to the river streams based on empirical equations; uses a lithological and soil  
480 description, as well as hydrology, as its input data. The SWATLitho model is not based on a spatial  
481 mineralogical representation but on lithological groups of minerals that are available worldwide (cf. Hartmann  
482 and Moosdorf, 2012) or commonly available in finer resolution for local studies. However, it lacks point  
483 source data (for irrigation, saline springs, or other anthropogenic inputs). In fact, even though the SWAT  
484 model has been widely applied (Fu et al., 2019), there may be occasions when it is not possible to set up the  
485 model even though there is interest exists in assessing the chemical weathering derived geochemical loadings  
486 in a dynamic way.

487 Applying the SWATLitho model to evaluate daily loadings at a local scale has yielded reasonable results for  
488 representing the dynamic ( $r^2 > 0.73$ ). However, applying the model to local-scale studies to quantify daily  
489 draining loads at the catchment's outlet is conditioned by a detailed representation of the area's lithology and  
490 the lack of other relevant salt sources. When considering the Altzola gauging station as a reference for the

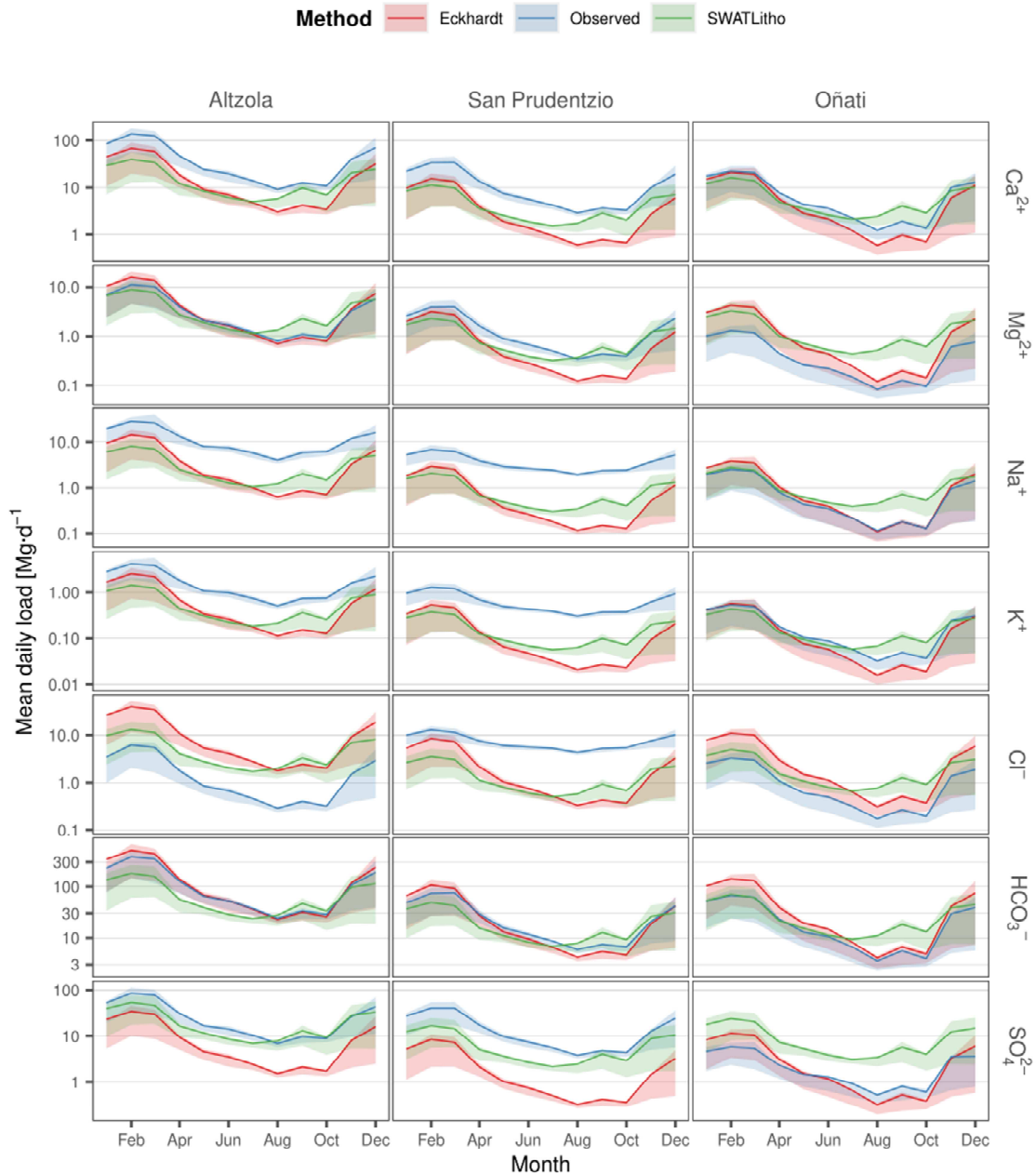
491 catchment-scale model application, the mean percentage of deviation of the model is ~-17.96% (Table 6). The  
492 results shown here do not include any variation in the mineral dissolution constant ( $c_{xi}$  in Equation 1) which is  
493 likely to occur with changes in groundwater or lateral flow water temperature. A more mechanistic model is  
494 needed to account for this evolution, as well as the chemical equilibrium between phases (as done in Bailey et  
495 al., 2019). However, the more mechanistic a model is, the harder it is to find available input data.

496 In the present study, a digital filter to deconvolute the hydrograph –distinguish surface runoff from baseflow  
497 and lateral flow with the total discharge time series– has been tested as a potential alternative when it is not  
498 possible to set up QSWATLitho projects, either because of a lack of input data or computational resources  
499 constraints. Interannual daily loads (mean, first, and third quartiles) are shown monthly in Figure 7. Spatial  
500 and temporal limitations of the SWATLitho model have been discussed in previous sections (3.1.3 and 3.1.4),  
501 but all three results in the Oñati drainage catchment, observed, SWATLitho and Eckhardt, present a similar  
502 temporal pattern. However, the SWATLitho presents a peak for all ions in September. This is not present in  
503 the other two methods, supporting the idea that the SWAT's groundwater flux computation is affected by  
504 pulses calculated in each HRU instead of a diffuse load, which is better represented by graphical separation in  
505 an Eckhardt model. Nonetheless, the variances of the two methods have yielded discrete values, though a  
506 Welch's test for the differences between the loadings SWATLitho and the Eckhardt module has yield a  
507  $p > 0.05$ , which does not demonstrate enough significance to indicate that the loadings are dissimilar. The  
508 visual inspection and the test demonstrate that the Eckhardt digital filter may be applied when a QSWATLitho  
509 project cannot be set up.

510 One of the limitations of the ICWR model is the presence of spring waters or point sources that alter the  
511 streams' composition. Those impacts are not presented in the model at this stage and should be considered  
512 when assessing the chemical loads from catchments with springs within their hydrogeological basin or  
513 groundwater inputs that are sourced outside the hydromorphological basin. When it comes to the model's  
514 performance from various input data, the greatest distinctions among results in the loadings have been found  
515 when changing the lithological map, yielding results closer to the observed values.

516 Future improvements of the SWATLitho model should allow the inclusion of saline point sources (which  
517 could represent natural saline springs or anthropogenic inputs), and permit the calibration of the  $c_{xi}$  parameters  
518 for each catchment (which could adjust the contribution of each lithology for each location) as done in the  
519 common SWAT calibration procedure.

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**Figure 7.** Average monthly inter-annual loading comparison among the observed, SWATLitho, and Eckhardt digital filter results. Lines indicate the mean value, while the shade represents the 1<sup>st</sup> and 3<sup>rd</sup> quartiles for the January 2014 to December 2017 time series. The vertical axis is shown in logarithmic scale.

525

## 4 Conclusion

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An empirical model used to estimate the annual average geochemical loads to rivers through chemical weathering has been downscaled from global to local scale, and shifted from an annual average estimation to a daily dynamic output, based on the coupling with SWAT, an extended hydrological model. The coupling method is described along with the case study, using different input datasets to check the influence of hydrology and lithology resolution in the outputs of the model. The use of globally fitted parameters for the model has yielded average loadings with a model underestimation of 17.96% with regards to the observed

532 data, though the model's performance is "reasonable" on the representation of spatially explicit daily  
533 geochemical loadings to stream the a catchment level.

534 The limitations of the model have been addressed, such as the poor performance of the model when springs  
535 are present in the study area, or when the lithological input dataset does not contain information  
536 hydrogeochemically relevant units, such as gypsum intrusions, which are too small to be mapped but relevant  
537 enough to affect the water chemistry and loadings. An alternative has also been presented for those cases in  
538 which a QSWATLitho project cannot be set up: the application of a digital filter to measure data in a gauging  
539 station, together with the drainage basin description (lithology and soil classes). The results do not present  
540 significant differences from those of the SWATLitho, which suggests that both methods may be applied when  
541 it is not possible to set the first one up or that spatially explicit results are not in the scope of the modelling.

542 The present work introduces a hydrogeochemical tool which is useful for estimating dynamic chemical  
543 weathering loadings out of a catchment at a local scale and also for the estimating of ionic fluxes that derive  
544 from the chemical weathering of rocks in a spatiotemporal context.

## 545 **Software availability**

- 546 • The Soil and Water Assessment Tool (SWAT) is freely available in <https://swat.tamu.edu/software/>
- 547 • The QGIS plugin for SWAT (QSWAT) is freely available in <https://swat.tamu.edu/software/qswat/>
- 548 • The modified QGIS plugin that is presented in this study (QSWATLitho) as well as the SWATLitho  
549 module written in Python are freely available in <https://swat.tamu.edu/software/swat-litho/>

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555 analysis, data curation, investigation, writing (original draft, review and editing), and in visualization; S.S.  
556 worked on the conceptualisation, methodology, validation, writing (review and editing), resources,  
557 investigation, supervision, and project administration; E.R.R. collaborated during the investigation, validation,  
558 resources, data curation, supervision, and funding acquisition; C.G. assisted with during the methodology,  
559 software, validation, resources, and writing (review and editing); J.M.S.P. supported during conceptualisation,  
560 methodology, software, validation, investigation, resources, writing (review and editing), supervision, and  
561 project administration.

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